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XVII.—ON CERTAIN SUBSTANCES OBTAINED FROM TURMERIC.

I.—CURCUMIN.[1]

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The chemical study of curcumin, the yellow coloring matter of turmeric, dates from a paper[2] by A. Vogel, Sr., and Pelletier, published in 1815, although even before this turmeric-paper had been used as a test for alkalies, and its action with boric acid and various salts observed.[3] No analysis is given in this paper, and the low melting-point (40°) and description of the method of preparation show that the "yellow coloring-matter of turmeric" obtained by Vogel and Pelletier was principally composed of resin and turmeric oil; they proved, however, that it contained no nitrogen, and studied its action with alkalies, acids, and certain salts, especially acetate of lead.

In 1842 A. Vogel, Jr.,[4] analysed a similar but perhaps somewhat purer preparation, which, however, must have consisted in great

[1] From the Proceedings of the American Academy. Communicated by the authors.

[2] Journal de Pharmacie **1**, 289.

[3] Trommsdorff, Trommsdorff's Journal von Pharm. **16**, 96. Sementini, Bibliothèque Britannique, Jan. 1815.

[4] Journ. de Pharm. et de Chim. sér. 3, **2**, 20.

part of the yellow resin contained in the root, as it also melted at 40°; it is not wonderful, therefore, that his analyses led to no formula.

Passing over a number of unimportant notices,[1] we come next to a paper by Schlumberger,[2] in which the action of a mixture of sulphuric and boric acids on crude curcumin is studied, and a description given of the product called by him rosocyanin, because it dissolved in alcohol with a fine red color, and was turned blue by alkalies. He also describes a resinous product of the action of boric acid on curcumin (pseudocurcumin).

Two years later, in 1868, Bolley, Suida, and Lange[3] examined the turmeric oil, and published a new analysis of a purer curcumin (melting-point 120°); but it was not till 1870 that curcumin was obtained essentially pure. In this year Daube,[4] Ivanow-Gajewsky,[5] and Kachler[6] published independent papers on the subject, of which Ivanow-Gajewsky's is entitled to the precedence, as the number of the Berlin Berichte which contained Daube's original paper gave a notice in the Correspondence of the reading of Gajewsky's paper before the Russian Chemical Society a month earlier. In addition to an analysis of the turmeric oil, he assigns, as the simplest possible, the formula C_4H_4O to curcumin, which after crystallization from ether or benzin melted at 172°. Daube, on the other hand, after extracting his curcumin with benzol, and purifying it by conversion into the lead salt, obtained the melting-point 165°, and the formula $C_{10}H_{10}O_3$. He also found that it was decolorized by sodium amalgam and alcohol, and converted into oxalic acid by dilute nitric acid.

Kachler, who did not succeed in crystallizing his curcumin, although both Ivanow-Gajewsky and Daube got crystals, obtained the same formula as the former, that is, C_4H_4O, or some multiple of it. He also studied the action of sodium amalgam upon it, and that of hot zinc dust, but with no very definite results in either case; whereas by fusing curcumin with potassic hydrate, he obtained

[1] Desfosses, Ann. Chim. Phys. **16**, 76; A. Vogel, Jr., Répert. Pharm. sér. 3, **3**, 178; H. Rose, Pogg. Ann. **102**, 545; Lepage, Archiv der Pharm. Ser. 2, **97**, 240; Leube, Vierteljahrsschr. pr. Pharm. **9**, 395; Alex. Müller, J. pr. Chem. **80**, 119; Wittstein, Vierteljahrsschr. pr. Pharm. **9**, 282; Schutzenberger, Paraf. Mul. Soc. Bull. 1861, 503; Ludwig, Archiv der Pharm. **106**, 169; Kraut, Zeitschr. anal. Chem. **4**, 168.

[2] Bull. Soc. Chim. sér. 2, **5**, 194.

[3] J. pr. Chem. **103**, 474.

[4] Berichte der deutschen chemischen Gesellschaft, **3**, 609.

[5] *Ibid.* **3**, 624.

[6] *Ibid.* **3**, 713.

protocatechuic acid. From the turmeric oil he obtained essentially the same analytical results as Ivanow-Gajewsky.

In 1872 Ivanow-Gajewsky published a second paper[1] on turmeric, containing another method for extracting curcumin, which, however, gave it a melting-point of 140°, and an analysis of the lead salt supporting his formula $C_{16}H_{16}O_4$ (=$(C_4H_4O)_4$). Moreover he confirmed the results of Kachler with fusing potassic hydrate (protocatechuic acid) and zinc dust, and states that the oil obtained with the latter is identical with turmeric oil, of which a new analysis is given, and its oxidation (yielding valeric and caproic acids) and action with phosphoric pentachloride studied. He also prepared and analysed rosocyanin, but was unable to find a satisfactory formula for it.

Finally, in 1873, he published the last paper[2] we have been able to find on this subject, in which he states that curcumin yields on oxidation with potassic dichromate terephthalic acid, and that rosocyanin contains no boron, and, fused with potassic hydrate, yields paraoxybenzoic acid.

In brief, the following facts had been established in regard to curcumin at the time that we began our research upon it:—Its formula was either $C_{10}H_{10}O_3$ or $C_{16}H_{16}O_4$; the highest melting-point observed was 172°; with alkalies it formed reddish-brown salts; with boric and sulphuric acids rosocyanin; it was susceptible of reduction, and gave an oil with zinc dust; by oxidation it yielded oxalic acid or terephthalic acid, and by fusion with caustic potash protocatechuic acid.

Accordingly we first turned our attention to the determination of its formula.

Extraction and Purification of Curcumin.

After several experiments we have adopted the following method as the best and most convenient:—The turmeric oil is first removed from the ground root by treatment with ligroine;[3] then the curcumin, mixed with a large quantity of resin, is extracted with ether, and finally purified by crystallization from alcohol.

The turmeric used by us has been principally Bengal turmeric, bought of Messrs. E. and F. King, of Boston; we have, however,

[1] Berichte der deutschen chemischen Gesellschaft, **5**, 1103. [2] *Ibid.* **6**, 196.

[3] In our first experiments we followed Ivanow-Gajewsky, and used carbonic disulphide for this purpose; but we have found that ligroine is not only much cheaper and more agreeable to work with, but yields a purer oil.

also extracted enough of the Madras turmeric, the only other brand occurring in the Boston market, to assure ourselves of the identity of the curcumin obtained from both.

For a full description and history of turmeric, which consists of the root-stocks of the *Curcuma longa*, a plant of the ginger family, growing in India and other parts of the East, we would refer to Flückiger and Hanbury's Pharmacographia,[1] and to a full botanical article recently published by A. Meyer[2] in the Archiv der Pharmacie.

The extracter was of the form recently described by Scheibler,[3] as this was the only one of which we have found a description adapted to the thorough extraction of large quantities of material; those forms in which the drug is not kept covered with the extracting liquid being apt to leave the edges partially unacted on. The only modification of Scheibler's apparatus made by us consisted in substituting a cylindrical tin vessel capable of holding 10 kil. of ground turmeric for the smaller glass vessel used by him. With a cooler 78 cm. long, the inner tube of which was a flattened U, also made of tin, the thorough extraction of the 10 kil. of turmeric could be accomplished in little more than a fortnight. The solvent was removed, after it had ceased to act, by forcing out as much as possible of it by air pressure, and then distilling off the rest by filling with steam a jacket which surrounded the vessel containing the turmeric.

The ligroine extract yielded on evaporation a dark yellow oil, amounting on the average to eleven per cent. of the weight of the root. The investigation of this substance will be described in a later paper.

The ether extract, a reddish-brown mass, varying in consistency from semi-liquid to solid according to the period of the extraction at which it was obtained, was treated with successive small quantities of cold alcohol, which dissolved the viscous impurities more easily than the curcumin. In very obstinate cases washing with ether was found advantageous; if, on the other hand, the extract was comparatively free from resin, it could be washed with alcohol upon a filter. In either case the residue was purified by recrystallization from alcohol until it showed the constant melting-point 178°.

[1] Macmillan and Co., London, 1879.
[2] Arch. Pharm. Ser. 3, **18**, 401.
[3] Berichte der deutschen chemischen Gesellschaft, **13**, 338.

The average yield of curcumin was 0.3 of one per cent.; this, however, is only the amount that can be extracted by the process just described; the quantity contained in the root is much larger, as a considerable amount remained mixed with the resinous impurities, and the green fluorescence of the crude turmeric oil pointed to the presence of some curcumin in this substance.

Composition of Curcumin.

The following combustions were made of the curcumin purified as just described and dried at 100°. In most of these analyses a slight ash was left, the amount of which has been subtracted from the weight of substance before calculating the percentages.

I. 0.1106 gram of substance gave 0.2774 gram of CO_2 and 0.0563 gram of H_2O. No ash.

II. 0.2180 gram gave 0.5450 gram of CO_2 and 0.1099 gram of H_2O. Ash 0.0007 gram.

III. 0.2149 gram gave 0.5376 gram of CO_2 and 0.1090 gram of H_2O. Ash 0.0006 gram.

IV. 0.2195 gram gave 0.5480 gram of CO_2 and 0.1099 gram of H_2O. Ash 0.0006 gram.

V. 0.2743 gram gave 0.6815 gram of CO_2 and 0.1378 gram of H_2O. Ash 0.0010 gram.

	I.	II.	III.	IV.	V.	Mean.
Carbon	68.43	68.39[1]	68.42[1]	68.27[1]	68.	30
Hydrogen	5.65	5.62	5.69	5.59	5.60	5.63

All these analyses were made with curcumin from Bengal turmeric: I. and II. of different portions of the same sample, III., IV., and V. of different samples.

The following analysis was made of curcumin extracted from Madras turmeric:

0.3467 gram gave 0.8612 gram of CO_2 and 0.1870 gram of H_2O. No ash.

Carbon	67.74
Hydrogen	5.99

[1] These numbers become, if the ash is not subtracted from the weight of the substance:

	II.	III.	IV.	V.
Carbon	68.17	68.23	68.09	67.75
Hydrogen	5.60	5.64	5.56	5.58

The sample analysed was very red, and the somewhat lower percentage of carbon obtained was undoubtedly due to the presence of an impurity which causes the curcumin to crystallize in red burrs, as is shown by the following analysis of a very red sample of Bengal curcumin:

0.2168 gram of substance gave 0.5400 gram of CO_2 and 0.1057 gram of H_2O. No ash.

Carbon	67.93
Hydrogen	5.42

It is to be observed, however, that enough of this impurity to change the crystalline habit and color of the curcumin has but a very slight effect on the percentage composition, and, it may be added, does not lower the melting point more than one degree. That it is formed by the oxidation of curcumin by the action of the air, appears from the fact that pure yellow curcumin was partially converted into red burrs when moistened with alcohol and exposed to the air for a long time. When once formed, the impurity can be removed only by repeated crystallization, and the amount of Madras curcumin at our disposal did not admit of this, nor did we take the trouble to prepare a larger supply, as the above analysis with the melting point 178° is sufficient to establish the identity of the Madras and Bengal curcumins.

The following comparison shows that our results agree tolerably well with those of Daube, but are entirely at variance with those of Kachler and Ivanow-Gajewsky. (As no analyses are given in the abstract of the latter's article, which alone is at our disposal, we have given the theory for his formula, $C_{16}H_{16}O_4$, under his name.)

	Ivanow-Gajewsky.	Kachler.		Daube.		Jackson and Menke Mean.	
Carbon	70.58	69.90	69.87	67.90	67.89	67.92	68.30
Hydrogen	5.90	5.70	5.59	5.66	5.76	5.70	5.63

There are, then, eight analyses of curcumin which support a percentage of carbon in the neighborhood of 68, against three (or more) in favor of one near 70.[1]

It is probable that the high results obtained by Ivanow-Gajewsky and Kachler were due to the presence of resinous impurities, since

[1] Ivanow-Gajewsky obtained a percentage of lead in a plumbic salt agreeing with his combustion; but this result is more than counterbalanced by the analyses of derivatives of curcumin given later in this paper.

their predecessors, who analysed exceedingly impure curcumin, as shown by the low melting point, obtained the following results:

	A. Vogel, Jr.	Bolley, Suida and Lange.
Carbon	69.50	69.07
Hydrogen	7.46	6.40

This view is further supported by the fact that we obtained a higher melting point, 178°, than any one else; Daube found 165°, Ivanow-Gajewsky 172°, later 140°, while Kachler gives no melting point, and did not succeed in obtaining his curcumin crystallized. In view of these facts we feel no hesitation in rejecting all the previous analytical results except those of Daube.

Daube gives curcumin the formula $C_{10}H_{10}O_3$, but our results, and for that matter his, agree much better with the formula $C_{14}H_{14}O_4$, as appears from the following comparison:

	$C_{10}H_{10}O_3$	$C_{14}H_{14}O_4$	Daube.	Jackson and Menke.
Carbon	67.42	68.29	67.90	68.30
Hydrogen	5.62	5.69	5.70	5.63

We have therefore adopted the formula $C_{14}H_{14}O_4$, which is also confirmed by the analyses of derivatives of curcumin to be given later in the paper.

Properties of Curcumin.

Curcumin crystallizes from alcohol in stout needles, which under the microscope appear as well-formed prisms with square ends, or spindle-shaped crystals, often arranged in radiating groups; in color it is orange to yellow, according to the size of the crystals, with a beautiful blue reflex; its solution in ether exhibits a very strong green fluorescence; when pure it has no odor; it melts at 178°, apparently with decomposition.[1] It is nearly insoluble in water, somewhat soluble in cold, more readily in hot alcohol and methyl alcohol, more soluble in glacial acetic acid than in alcohol, less so in ether, very slightly soluble in benzol[2] and carbonic disulphide, and essentially insoluble in ligroine. Strong sulphuric acid dissolves it with a fine reddish-purple color, which changes to black from charring after some time; strong hydrochloric acid produces the same effect, but with more difficulty. It is readily sol-

[1] Daube found 164°; Gajewsky, 172° or 140°.

[2] Compare Daube, Berichte der deutschen chemischen Gesellschaft, **3**, 609.

uble in alkalies and alkaline carbonates, and is even dissolved to a slight extent when boiled with precipitated calcic carbonate and water. The solution in ammonic hydrate loses ammonia when boiled, and deposits unaltered curcumin. A solution of baric hydrate converts it into a blackish-red powder, but lime-water gives a red solution like that obtained from calcic carbonate. It is not affected by acid sodic sulphite.

Salts of Curcumin.

In taking up the study of this subject we were at first attracted to the lead salt by the analyses and descriptions of Ivanow-Gajewsky and Daube; but, after several experiments, we decided that it was too indefinite a substance to throw much light upon the nature of curcumin, and accordingly turned our attention to the potassium salts, which at first did not seem promising, but on proper treatment have yielded satisfactory results. Before describing these, however, we will say, that there seem to be at least two lead salts, as we have obtained a dark claret precipitate and also a flame-colored one. The most promising method of preparation seemed to be boiling curcumin with precipitated calcic carbonate and water, and adding plumbic acetate to the filtrate; in this way the flame-colored salt was obtained.

We have succeeded in obtaining two potassium salts, containing one and two atoms of potassium respectively.

Dipotassic Salt of Curcumin $K_2C_{14}H_{12}O_4$.

This was made by adding a large excess of a strong alcoholic solution of potassic hydrate to a hot saturated solution of curcumin in alcohol; if the solutions are strong enough, flame-colored crystals of the salt are deposited on cooling; if this is not the case, it can be precipitated by addition of ether. If an insufficient amount of potassic hydrate is used, a dark red solution of the monopotassic salt is formed, which becomes lighter on the addition of more potassic hydrate as the second atom of potassium is taken up. The salt was crystallized from boiling alcohol to which a few drops of ether had been added, washed with a mixture of alcohol and ether, then with ether alone, pressed on filter-paper, and dried as rapidly as possible in a steam-drying closet containing some potassic hydrate.

0.7168 gram of the salt gave, heated with sulphuric acid, 0.3824 gram of K_2SO_4.

0.2675 gram gave 0.1459 gram of K_2SO_4.

	Calculated for $C_{14}H_{12}K_2O_4$	Found.	
Potassium	24.27	23.95	24.48

If curcumin had the formula $C_{16}H_{16}O_4$ the dipotassic salt would contain—

Potassium 22.46.

The salt consists when first formed of flame-colored needles in globular radiating groups, but becomes deep claret on drying. It is freely soluble in water, not quite so soluble in alcohol, and essentially insoluble in ether; the alcoholic solution takes on a magenta color when exposed to the air, and the salt seems to absorb carbonic dioxide readily, although the change of color was more probably due to oxidation.

Monopotassic Salt of Curcumin $KC_{14}H_{13}O_4$.

If an excess of potassic carbonate is added to a hot solution of curcumin in absolute alcohol, there is a violent effervescence, and the liquid turns deep blood red. After slight concentration the excess of potassic carbonate was removed by filtration, the salt precipitated with ether, and purified by washing with ether. An attempt to crystallize it from a mixture of alcohol and ether gave no satisfactory result. Pressed between filter-paper, and then dried at 100°, it gave the following results:

I. 0.4808 gram of the salt gave after ignition with sulphuric acid 0.1540 gram of K_2SO_4.

II. 0.5381 gram of salt gave 0.1680 gram of K_2SO_4.

	Calculated for $KC_{14}H_{13}O_4$	Found.	
		I.	II.
Potassium	13.76	14.36	14.02

$KC_{16}H_{15}O_4$ contains 12.60 per cent. of potassium.

This salt is precipitated in crimson black flocks, which dry to a mass having the green color and lustre of rosanilin, although the shade is somewhat blacker. It is very easily soluble in water and alcohol, giving blood-red solutions, but insoluble in ether, and does not seem to be altered by exposure to the air. It can also be made by the action of an excess of curcumin on the dipotassic salt, or by

adding potassic hydrate not in excess to curcumin suspended in alcohol. It is very much more soluble than the dipotassic salt.

Curcumin forms also a flame-colored calcium salt, slightly soluble in water, which can be made by adding calcic chloride to a solution of the monopotassic salt. The same salt is formed in small quantity when calcic carbonate is boiled with curcumin and water or alcohol, carbonic dioxide being set free.

The zincic salt seems to be soluble, the baric salt insoluble,[1] while the silver salt is probably very unstable, as curcumin is decomposed when boiled for more than a minute with argentic nitrate and alcohol.

The fact that only one atom of the hydrogen contained in curcumin can be replaced by the potassium of potassic carbonate would point to the existence of one, and only one, carboxyl group in its molecule; the presence of this group is confirmed farther by the power of decomposing calcic carbonate possessed by curcumin.[2] The replacement of a second atom of hydrogen when curcumin is treated with potassic hydrate in excess indicates the existence of a hydroxyl group, probably a phenol hydroxyl, and it would seem, therefore, that curcumin is a diatomic monobasic acid.

Esters of Curcumin.

Although the analyses of the potassium salts had agreed with the formula of curcumin derived from the analysis of the original substance, it seemed desirable to confirm this formula still farther by the study of some derivative of curcumin more stable and easily handled than the salts; we accordingly took up the investigation of the esters, but found that the ethyl ester made by the action of ethyliodide on the dipotassic salt was a disagreeable brownish-black tarry substance, that could not be obtained in a crystalline condition. We therefore abandoned the study of this substance and turned our attention to the monoparabrombenzyl ester, which we preferred to the benzyl ester, in the first place because of the great tendency of the parabrombenzyl compounds to crystallize, and secondly, since the presence of bromine increased the difference

[1] As our work on the potassium salts had achieved the end for which we undertook the study of the salts of curcumin, we thought it not worth while to purify any of the other salts for analysis.

[2] Some experiments on the action of phosphorus trichloride upon monoethylcurcumin confirmed the presence of a carboxyl group, so far as they went, but the product was too ill-defined to repay a thorough study.

between the percentages of carbon in the two formulas by more than five-tenths of one per cent., and also gave a third element whose quantity could be determined.

Monoparabrombenzyl Ester of Curcumin $C_{14}H_{13}(C_7H_6Br)O_4$.

To an alcoholic solution of the monopotassic salt of curcumin an excess of parabrombenzylbromide was added, and the mixture allowed to stand for several days, when it was found that pale yellow crystals mixed with potassic bromide had been deposited; the dark-colored liquid was poured off, and the solid residue freed from parabrombenzylbromide by repeated treatment with hot ligroine, and from curcumin by boiling with successive portions of aqueous potassic carbonate, until it ceased to give a red solution. The essentially pure ester thus obtained was boiled several times with alcohol, which dissolved a small portion of it, while the residue melted to a reddish-black tar; upon dissolving this in glacial acetic acid and precipitating with water, yellowish flocks were thrown down, the melting point of which was compared with that of the similarly-colored indistinct crystals obtained by cooling the alcoholic extract. As both these substances melted, or, more accurately, drew together, at the same temperature, the ester seemed to be essentially pure, and after drying at 50°-60° was analysed.

I. 0.1796 gram of substance gave 0.3980 gram of CO_2 and 0.0817 gram of H_2O.

II. 0.2506 gram of substance gave according to Carius 0.1156 gram of AgBr.

	Found.	Calculated for $C_{14}H_{13}(C_7H_6Br)O_4$	$C_{14}H_{13}(C_7H_6Br)O_4$
Carbon	60.43	60.72	62.58
Hydrogen	5.05	4.57	4.76
Bromine	19.63	19.26	18.14

From these results there can be no doubt that $C_{14}H_{14}O_4$ is the true formula of curcumin.

The ester consists of indistinct crystals, grouped in forms like cauliflowers, of a much paler yellow color than curcumin; it melts at 76°–78°, beginning to draw together at 76°, and becoming thoroughly liquid at 78°; we have not succeeded in obtaining it with a perfectly sharp melting-point. It is more soluble in glacial acetic acid than in alcohol, nevertheless the latter is to be preferred

as a solvent for obtaining crystals, since the substance is apt to separate from the hot glacial acetic acid in a fused tarry condition. It is readily soluble in ether and benzol, but does not crystallize well from these solvents; slightly soluble in carbonic disulphide; essentially insoluble in ligroine; not attacked by a solution of potassic carbonate, but soluble in potassic hydrate, although without the red color charcteristic of curcumin. As the analysis of this ester establishes our formula, we have not continued the study of the esters.

Oxidation of Curcumin.

Our experiments on this subject can be divided into two classes, those in which we made a complete oxidation of the substance, and those in which a partial oxidation was obtained by using an insufficient amount of the oxidizing agent, or one less energetic.

Complete Oxidation.—As Ivanow-Gajewsky states that he obtained terephthalic acid by the action of potassic dichromate and sulphuric acid on curcumin, we turned our attention first to this experiment. Unfortunately only an abstract of his paper is accessible to us, so that we could not find the exact conditions of his oxidation; we have therefore varied the conditions in several ways, but always with the same result. It will be sufficient to describe a single experiment. Half a gram of curcumin was mixed with sulphuric acid previously diluted with its own volume of water, and solid potassic dichromate added; the action was extremely violent, accompanied by great evolution of heat and strong effervescence; the gas given off was carbonic dioxide. At the end of the process there was no insoluble substance in the liquid, which was therefore distilled until it was reduced to a small volume. The strongly acid distillate, treated with argentic oxide, after filtering and concentration, deposited long flattened needles, which looked exactly like argentic acetate, and were proved to consist of this substance by the following silver determination:

0.1812 gram of salt dried at 100° gave 0.1559 gram of AgCl.

	Calculated for $AgC_2H_3O_2$	Found.
Silver	64.68	64.76

There was no other volatile acid in the distillate, and no organic matter could be found in the residue from the distillation. If the action was moderated by using more dilute sulphuric acid, the

phenomena were the same, except that it was necessary to start the reaction by the aid of heat. In none of the products of the oxidation of curcumin with potassic dichromate could any terephthalic acid be found, they consisted only of acetic acid and carbonic dioxide.

If curcumin is dropped into fuming nitric acid it dissolves with a hissing noise and formation of nitrous fumes and hydrocyanic acid. The red liquid thus obtained gave no precipitate with water; on evaporation it deposited brownish crystals, principally oxalic acid, but it was not further examined. In this respect we confirm the results of Daube, who also obtained oxalic acid from curcumin and nitric acid.

Incomplete Oxidation.—When curcumin was dissolved in aqueous potassic hydrate, a solution of potassic permanganate added, not in excess, and after the oxidation had ceased, the liquid acidified with sulphuric acid, a strong smell of vanilla was observed. The liquid was accordingly filtered, and the precipitate thoroughly washed with boiling water, the filtrate and wash-water extracted with ether, and the extract treated with acid sodic sulphite, as directed by Tiemann and Haarmann.[1] The product was an oil, having a strong smell of vanilla and gradually solidifying in circular groups of radiating needles; the amount, however, was extremely small, and none of this product was obtained with an excess of potassic permanganate or when the quantity of curcumin was much more than half a gram. The same substance was obtained with various weak oxidizing agents, such as bleaching powder and water, potassic ferricyanide with potassic hydrate, and even the action of atmospheric oxygen on curcumin dissolved in potassic hydrate. Of these the mixture of potassic hydrate and potassic ferricyanide gave the best yield, but even this was extremely small—in fact, after uniting the product from all the oxidations made by us, in which over eight grams of curcumin were used, the quantity was not enough for complete purification. By sublimation, however, and subsequent crystallization from boiling water, it was obtained in white needles resembling in appearance and odor the vanillin from the vanilla-bean and melting at 79°. Vanillin melts at 80°–81°.

In addition to the vanillin there were formed carbonic dioxide, a black amorphous substance with feebly acid properties, perhaps

[1] Berichte der chemischen Gesellschaft, **8**, 1115.

the aldehyd resin of vanillin, as it appeared in largest quantity when no vanillin was obtained, and an acid volatile with steam. We have not as yet made any complete study of these secondary products, because the properties of the humus-like substance are far from inviting, and the amount of the volatile acid is so minute that its isolation in quantity sufficient for analysis would be extremely laborious. We shall, however, return to these substances if we fail in finding easier methods for studying the nature of the side-chain.

As the small yield of vanillin was undoubtedly due to the presence of the phenol hydroxyl, which offered a point of attack for the oxidizing mixture, we next tried to increase our yield by replacing the hydroxyl hydrogen with some radical which would protect it from oxidation, and in this way not only prove that the substance was really vanillin, but also that it was one of the principal products of the oxidation. For this purpose we first tried to make acetylcurcumin by treating curcumin with acetylchloride; this gave a deep bluish-green liquid, which on standing turned brown, and then yielded on addition of water a yellowish precipitate which could not be obtained in crystals, its solutions forming on evaporation a dark-colored varnish. With acetic anhydride no better results were obtained, and as there seemed no prospect of getting a good analysis of the substance, it was at once oxidized with potassic permanganate. The result was not essentially better than that obtained with pure curcumin, and we accordingly turned our attention to the oxidation of diethylcurcumin, which was made by boiling the dipotassic salt with absolute alcohol and a slight excess of ethyliodide for six hours in a flask with a return cooler. On distilling off part of the alcohol and allowing the rest to evaporate spontaneously, the compound is left as a most uninviting brownish-black tar, which when heated with sodic hydrate dissolves with a dark red color resembling that of the alkaline solution of curcumin. Upon treating this solution with potassic permanganate until it was decolorized, filtering from manganic hydrate, and acidifying with sulphuric acid, a yellowish precipitate was obtained, which after two crystallizations from boiling water with bone-black melted at 195°, the melting point given by Wassermann[1] for ethylvanillic acid (Tiemann[2] gives 193°–194°).

[1] Annalen der Chemie, **179**, 366.
[2] Berichte der deutschen chemischen Gesellschaft, **8**, 1127.

The nature of the substance was still further confirmed by the following combustion:

0.1216 gram of substance gave 0.2714 gram of CO_2 and 0.0707 gram of H_2O.

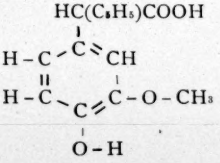
	Calculated for $C_{10}H_{12}O_4$	Found.
Carbon	61.22	60.87
Hydrogen	6.12	6.46

There can be no doubt, therefore, that the substance is ethylvanillic acid, and it was formed in such quantity that it must be considered one of the principal products of the reaction. If the potassic permanganate was not added in excess, and the liquid extracted with ether, crystals of ethylvanillin were obtained, which on sublimation formed an oil solidifying after a short time in large twinned crystals like those of cassiterite, and having a smell similar to that of vanillin, but not identical with it.

Summary of Results.

The formula of curcumin is $C_{14}H_{14}O_4$, as proved by analyses of curcumin itself, of its potassium salts, and its parabrombenzyl ester.

It is a phenol-carboxylic acid, as shown by the study of its salts. The presence of carboxyl is indicated by its power of driving carbonic acid out of potassic and calcic carbonates, and by the decomposition of its diethylester on boiling with potassic hydrate. It contains the vanillin group, and therefore its formula, as far as we have determined it, is:



We are at present engaged in the study of the group C_6H_5, and propose to extend our investigations to rosocyanin and the turmeric oil.

XVIII.—DIBROMIODACRYLIC AND CHLORBROMIODACRYLIC ACIDS.[1]

By Charles F. Mabery and Rachel Lloyd.

From the ease with which various substituted acrylic acids have been obtained from brompropiolic acid,[2] we were led to believe that derivatives of some interest would result by the simultaneous addition of different halogens. This idea was confirmed by a few preliminary experiments, which showed that iodine monobromide and iodine monochloride could readily be made to form addition-products with brompropiolic acid. These substances have been submitted to a careful study, and the results we have obtained are presented in this paper.

Dibromiodacrylic Acid.

Dibromiodacrylic acid was made from brompropiolic acid, by the action of iodine monobromide. In the preparation of iodine monobromide according to the method of Lagermarck,[3] the required weight of iodine, with an excess of bromine, was heated to 50° for ten minutes on the water-bath. Dibromiodacrylic acid was formed in small quantity, when the solid residue left by evaporation of the excess of bromine was dissolved in ether and allowed to stand with brompropiolic acid. The product of this reaction, however, consisted to a large extent of an oil, from which very little pure substance could be recovered. This difficulty was partially overcome by the application of heat; and by boiling the solution for an hour on the water-bath we succeeded in obtaining about forty per cent. of the amount theoretically required. The thick pasty mass left after the evaporation of the ether soon solidified, and was easily purified by crystallization from hot water.

Dibromiodacrylic acid dissolves readily in ether, alcohol, carbonic disulphide and chloroform. In cold water it is rather sparingly soluble; from a concentrated hot solution it falls at first as an oil, which crystallizes as the solution cools, in oblique prisms of the

[1] The investigations described in the following papers were made under my supervision, and they formed a part of the work in the Summer Course of Instruction in Chemistry for 1881.—C. F. Mabery.

[2] Proceedings American Academy, **16**, 211, 235.

[3] Berichte der deutschen chemischen Gesellschaft, **7**, 907.

monoclinic system. It melts at 139°–140°, and sublimes slowly at higher temperatures.

The composition of this substance was determined by the following analyses:

I. 1.0762 gram of the substance gave 0.3385 gram CO_2 and 0.0420 gram H_2O.

II. 0.1993 gram of the substance gave by the method of Carius 0.3385 gram AgBr+AgI.

	Calculated for $C_3HBr_2IO_2$.	Found. I.	Found. II.
C	10.11	9.85	...
H	.28	.43	...
2Br+I	80.63		80.21

To determine the solubility of this acid at ordinary temperatures, we used the method of V. Meyer. The filtered solution was neutralized with baric carbonate, and the barium estimated by precipitation with sulphuric acid.

I. 8.7164 grams solution gave 0.0968 gram $BaSO_4$.

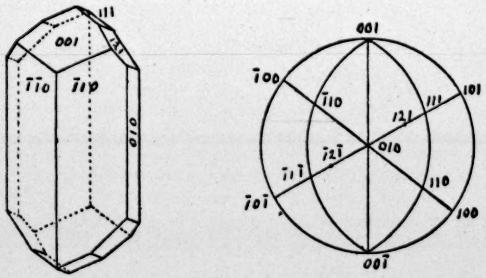
II. 9.7772 grams solution gave 0.1089 gram $BaSO_4$.

The solution saturated at 20° contains, therefore, the percentages:

I.	II.
3.39	3.40

Dr. W. H. Melville has made a crystallographic examination of this substance, and obtained the following results:

CRYSTALLINE FORM OF DIBROMIODACRYLIC ACID.



MONOCLINIC SYSTEM.

Forms [001], [010], [110], [121], [111].[1]

Elements:—Clinodiagonal, $a = 0.617$
Orthodiagonal, $b = 1.$
Vertical Axis, $c = 0.581$
Angle of Axes $= 52° 11\frac{1}{2}'$

		Observed.	Calculated.
Angles between normals	001 and 110	123° 26′	Fundamental angles.
	110 " 010	64°	
	111 " 110	59° 14½′	
	111 " 010	62° 11′	61° 47′
	121 " 010	42° 59′	42° 58′
	121 " 001	70° 29′	70° 19′
	121 " 110	55° 59′	56° 13′
	121 " $\bar{1}10$	84° 55′	85° 5½′

The following salts of this acid have been examined:

Baric dibromiodacrylate $Ba(C_3Br_2IO_2)_2.3\frac{1}{2}H_2O$.

To prepare the barium salt, a solution of the acid was neutralized with baric carbonate and the filtered solution concentrated by evaporation. On cooling the salt crystallized in rhombic prisms, which were very soluble in hot, less soluble in cold water. The air-dried salt lost three and a half molecules of crystal water at 80°.

I. 0.7087 gram of the air-dried salt lost 0.0512 gram H_2O at 80°.
II. 0.7273 gram of the salt lost 0.0535 gram H_2O at 80°.
III. 0.6244 gram of the salt lost 0.0441 gram H_2O at 80°.
IV. 0.6575 gram of the anhydrous salt gave 0.1808 gram $BaSO_4$.

	Calculated for $Ba(C_3Br_2IO_2)_2.3\frac{1}{2}H_2O$.	Found.		
		I.	II.	III.
$_2O$	6.92	7.23	7.36	7.06

	Calculated for $Ba(C_3Br_2IO_2)_2$.	Found.
	16.17	16.16

T. solubility of this salt in cold water was determined by V. Meye.'s method. The saturated solution was filtered, evaporated to dryness, and the barium estimated by ignition with sulphuric acid.

[1] The form [111] appeared only on a few crystals.

I. 2.6342 grams of a solution saturated at 20° gave 0.1038 gram $BaSO_4$.

II. 2.0175 grams of a solution saturated at 20° gave 0.0806 gram $BaSO_4$.

From these determinations the following percentages were calculated:

I.	II.
14.32	14.52

Calcic dibromiodacrylate $Ca(C_3Br_2IO_2)_2$.

The calcium salt was made by saturating an aqueous solution of the acid with calcic carbonate. From the concentrated solution the salt crystallized in clustered needles which were less soluble in cold than in hot water. When air-dried it was constant at 80°.

0.4118 gram of the salt dried at 80° gave 0.0714 gram $CaSO_4$.

	Calculated for $Ca(C_3Br_2IO_2)_2$.	Found.
Ca	5.33	5.10

Potassic dibromiodacrylate $KC_3Br_2IO_2$?

This salt was prepared by neutralizing an aqueous solution of the acid with potassic carbonate and evaporating on the water-bath. It separated in the form of rhombic plates, which proved to be so deliquescent that we were unable to determine the water of crystallization.

0.8834 gram of the salt dried at 80° gave 0.1842 gram K_2SO_4.

	Calculated for $KC_3Br_2IO_2$.	Found.
K	9.92	9.92

Argentic dibromiodacrylate $AgC_3Br_2IO_2$.

From a hot aqueous solution of the acid the silver salt is precipitated by the addition of argentic nitrate in hexagonal plates. It may be recrystallized from hot water without decomposition, and it is but slightly affected by the action of light. The salt was dried over sulphuric acid for analysis.

1.0737 gram of the salt gave by precipitation with HBr 0.4288 gram AgBr.

	Calculated for $AgC_3Br_2IO_2$.	Found.
Ag	23.32	22.98

When dibromiodacrylic acid is heated to 100° in a closed tube with bromine, iodine is set free and bromine takes its place. The substance thus formed is identical with the tribromacrylic acid described by Professor H. B. Hill and one of us[1] as shown by its melting point 115°–118°, and by a study of its crystalline form. The following angles were measured by Dr. Melville:

	Angles between normals.	Tribromacrylic acid from dibromiodacrylic.	Tribromacrylic acid from brompropiolic.
Zone [010, 110]	110 and 010	65° 33′	65° 38′
	010 " $\bar{1}10$	65° 44	
	$\bar{1}10$ " $\bar{1}\bar{1}0$	48° 28′	48° 40′
	$\bar{1}10$ " $0\bar{1}0$	65° 52½′	
	$0\bar{1}0$ " 110	65° 35′	
	$1\bar{1}0$ " 110	48° 44′	
		359° 56½′	
Zone [010, 011]	010 and 011	63° 11′	63° 14′
	011 " 011	54° 5′	53° 33′
	$0\bar{1}1$ " $0\bar{1}0$	62° 56′	

It also gave the percentage of bromine required for tribromacrylic acid.

0.1553 gram substance gave 0.2819 gram AgBr.

	Calculated for $C_3HBr_3O_2$.	Found.
Br	77.66	77.25

Chlorbromiodacrylic Acid.

Chlorbromiodacrylic acid may be prepared most conveniently by heating brompropiolic acid with an ethereal solution of iodine monochloride, although without the application of heat the reaction takes place slowly. Iodine monochloride was made according to the method proposed by Bunsen.[2] The calculated weight of iodine was dissolved in aqua regia with the aid of heat, and after cooling the solution was extracted with ether and washed thoroughly with water. When brompropiolic acid is heated for an hour with this solution, the oily liquid left on evaporation of the ether soon deposits large prismatic crystals of the addition-product. For purification the crude product was pressed in filter-paper and recrystallized from hot water.

[1] Proceedings American Academy, **16**, 216.

[2] Annalen der Chemie, **74**, 8.

This substance is readily soluble in ether and alcohol, somewhat less so in carbonic disulphide and chloroform. From a hot aqueous solution it separates as an oil which crystallizes on cooling in rhombic prisms of the monoclinic system. By crystallization from water we did not succeed in raising the melting point above 110°; but the crystals formed by slow evaporation of a solution in carbonic disulphide melted at 115°–116°. It sublimes freely at somewhat higher temperatures.

This acid was identified by the following analyses:

I. 0.6743 gram substance gave 0.2843 gram CO_2.[1]

II. 0.1505 gram substance gave 0.2721 gram AgCl+AgBr+AgI.

	Calculated for $C_3HClBrIO_2$.	I.	II. Found.
C	11.55	11.50	
H	.32		
Cl+Br+I	77.84		77.41

The following results were obtained in determining the solubility in cold water:

I. 8.1470 grams of a solution saturated at 20° gave 0.1396 gram $BaSO_4$.

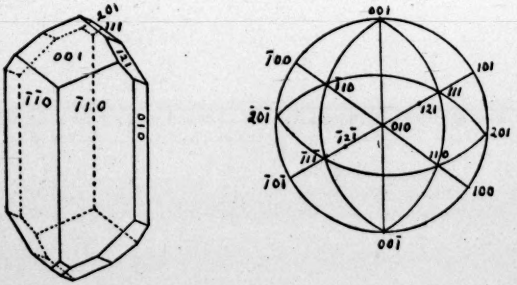
II. 5.4630 grams of a solution saturated at 20° gave 0.0968 gram $BaSO_4$.

From these results were calculated the percentages:

I.	II.
4.58	4.74

For a determination of the crystalline form of this acid we are indebted to the kindness of Dr. Melville, who obtained the following results:

Crystalline Form of Chlorbromiodacrylic Acid.



[1] By an accident the water in this combustion was lost.

MONOCLINIC SYSTEM.

Forms [001], [010], [110], [121], [111], [201].

Elements:—Clinodiagonal, $a = 0.594$
Orthodiagonal, $b = 1$.
Vertical Axis, $c = 0.572$
Angle of axes XZ $= 52° 47'$

			Observed.	Calculated.
Angles between normals	111 and	110	58° 23′	Fundamental angles.
	121 "	110	55° 45′	
	121 "	101	43° 48′	
	111 "	010	62° 43′	62° 28′
	110 "	001	123° 26′	123° 13′
	110 "	010	65° 3′	64° 56′
	111 "	110	82° 24′	82° 23′

It will be seen by inspection of the forms of dibromiodacrylic and chlorbromiodacrylic acids that these substances present a striking instance of isomorphism. In fact the only form not common to both is that of [201], which was not observed on the crystals of dibromiodacrylic acid. This similarity in form, which extends also to tribromacrylic acid, is rendered more prominent by a comparison of the observed angles. The measurements of tribromacrylic acid show a greater variation in the observed angles except in case of the angle which the prism [110] makes with the pinacoid [010].

	Dibromiod-acrylic acid.	Chlorbromiod-acrylic acid.	Tribrom-acrylic acid.
110 and 010	64° 3′	65° 3′	65° 33
110 " 110	128°	130° 6′	
110 " 001	123° 26′	123° 26′	
111 " 010	62° 11′	62° 43′	
111 " 110	59° 14½′	58° 23′	
121 " 010	42° 59′	43° 48′	
121 " 110	55° 59′	55° 45′	

The elements of the crystals also proved to be nearly identical.

	Dibromiod-acrylic acid.	Chlorbromiod-acrylic acid.
Clinodiagonal *a*	0.617	0.594
Orthodiagonal *b*	1.	1.
Vertical axis *c*	0.581	0.572
Angle of axes XZ	52° 11½′	52° 47′

A study was made of some of the more important salts of chlorbromiodacrylic acid.

Baric chlorbromiodacrylate $Ba(C_3ClBrIO_2)_2.3\frac{1}{2}H_2O$.

A solution of the acid was saturated with baric carbonate, filtered, and concentrated on the water-bath. The salt separated on cooling in rectangular prisms, which, when dried by exposure to the air, contained three and a half molecules of crystal water. It is quite soluble in cold, and very soluble in hot water.

I. 0.8250 gram of the air-dried salt lost when heated to 80° 0.0636 gram H_2O.

II. 0.7273 gram of the air-dried salt lost at 80° 0.0540 gram H_2O.

III. 0.5401 gram of the air-dried salt lost at 80° 0.0384 gram H_2O.

IV. 0.5502 gram of the air-dried salt lost at 80° 0.0438 gram H_2O.

V. 0.6697 gram of the anhydrous salt gave on ignition with H_2SO_4 0.2080 gram $BaSO_4$.

VI. 0.5032 gram of the anhydrous salt gave 0.1570 gram $BaSO_4$.

VII. 0.4959 gram of the anhydrous salt gave 0.1527 gram $BaSO_4$.

Calculated for $Ba(C_3ClBrIO_2)_2.3\frac{1}{2}H_2O$.		Found.			
		I.	II.	III.	IV.
H_2O	7.67	7.71	7.44	7.11	7.96

Calculated for $Ba(C_3ClBrIO_2)_2$.		Found.		
		V.	VI.	VII.
Ba	18.07	18.26	18.34	18.10

The solubility at 20° was determined by evaporating a saturated solution to dryness and igniting the residue with sulphuric acid.

I. 3.7500 grams solution gave 0.2339 gram $BaSO_4$.

II. 3.1458 grams solution gave 0.1957 gram $BaSO_4$.

According to these determinations a solution saturated at 20° contains the percentages:

I.	II.
20.30	20.23

Calcic chlorbromiodacrylate $Ca(C_3ClBrIO_2)_2.H_2O$.

When a solution of the acid is neutralized with calcic carbonate, and the filtered solution concentrated by evaporation, the calcium

salt separates in the form of branching needles. The air-dried salt contains one molecule of crystal water, which it loses at 80°.

I. 0.7180 gram of the air-dried salt lost 0.02116 gram H_2O at 80°.

II. 0.6770 gram of the air-dried salt lost 0.0197 gram H_2O at 80°.

III. 0.6583 gram of the anhydrous salt gave 0.1404 gram $CaSO_4$.

	Calculated for $Ca(C_3ClBrIO_2)_2.H_2O$.	Found. I.	II.
H_2O	2.66	3.01	2.91

	Calculated for $Ca(C_3ClBrIO_2)_2$.	Found. III.
Ca	6.05	2.91

Potassic chlorbromiodacrylate $KC_3ClBrIO_2$?

The potassium salt is obtained as a very deliquescent solid mass by evaporating a solution of the acid after neutralizing with potassic carbonate.

0.8076 gram of the salt dried at 80° gave on ignition with H_2SO_4 0.2176 gram K_2SO_4.

	Calculated for $KC_3ClBrIO_2$.	Found.
K	11.19	11.27

Argentic chlorbromiodacrylate $AgC_3ClBrIO_2$.

The silver salt was prepared by the addition of argentic nitrate to a hot aqueous solution of the acid. It crystallizes in rhombic prisms, which are quite soluble in hot, sparingly soluble in cold water.

I. 0.5383 gram of the salt gave 0.1825 gram AgCl.

II. 0.5129 gram of the salt gave 0.1766 gram AgCl.

	Calculated for $AgC_3ClBrIO_2$.	Found. I.	II.
Ag	25.80	25.52	25.91

XIX.—PRELIMINARY NOTICE OF ORTHOIODBENZYLBROMIDE AND ITS DERIVATIVES.[1]

By Charles F. Mabery and Franklin C. Robinson.

Orthoiodbenzylbromide is formed when bromine is allowed to act on orthoiodtoluol at temperatures near its boiling point. In the preparation of orthoiodtoluol we obtained the most satisfactory results from the sulphate of orthodiazotoluol. Orthotoluidin from the factory of Kahlbaum at Berlin was treated in quantities of 10 grams each, with two molecules of sulphuric acid, and to this mixture (cooled to 0°) was added gradually a solution of one molecule of sodic nitrite. On the addition of hydriodic acid (boiling point 127°) in slight excess over the calculated amount for the solution of the diazo-compound thus obtained, orthoiodtoluol was precipitated as a heavy oily liquid. The crude product was washed with sodic hydrate and acetic acid, and lastly with water. It was then dried over calcic chloride, and finally purified by fractional distillation. In this way from 20 grams orthotoluidin we obtained before fractioning 28 grams orthoiodtoluol, which gave 20 grams boiling at 211° (mercury column wholly in vapor).[2]

To convert orthoiodtoluol into orthoiodbenzylbromide, 10 grams were heated to 190°–200° under a return condenser, and 10 grams bromine allowed to run into the flask from a drop funnel as rapidly as it was absorbed. On cooling, the product of the reaction formed a thick oily liquid which did not solidify at 0°. It was therefore washed with a dilute solution of sodic hydrate, to remove the iodine which was invariably set free during the bromiring, and distilled in the vapor of concentrated hydrobromic acid according to the method followed by Professor Jackson in the purification of orthobrombenzylbromide.[3] The distillate solidified when cooled with snow, and after removing the oil by pressure in filter-paper, it purified by crystallization from ligroin.

The composition of this substance was established by the following analyses:

I. 0.1994 gram of the substance gave 0.3945 gram AgBr+AgI.

[1] Since Professor Jackson decided not to include orthoiodbenzylbromide in his researches on the substituted benzyl compounds, we have undertaken its study.—(C. F. M.)

[2] Kekulé, Berichte der deutschen chemischen Gesellschaft, **7**, 1007.

[3] Proceedings American Academy, **12**, 217.

II. 0.2793 gram of the substance gave 0.3945 gram AgBr+AgI.

III. 0.3246 gram of the substance gave 0.3350 gram CO_2 and 0.0674 gram H_2O.

	Calculated for C_7H_6BrI.	Found.		
		I.	II.	III.
C	28.28			18.16
H	2.02			2.30
Br+I	69.68	69.53	69.11	

Orthoiodbenzylbromide is readily soluble in ether, hot alcohol, benzol, carbonic disulphide, and chloroform. It is nearly, if not quite, insoluble in water, and very sparingly soluble in cold ligroin. From a cold saturated solution in ligroin it crystallizes by slow evaporation in flattened prisms often 2 or 3 centimeters in length. When crystallization takes place from a hot solution it appears in the form of short thick prisms. The vapor of this substance affects the mucous membrane in the same way as that of all the benzyl compounds thus far examined, and it seems to be far more volatile than the corresponding para compound. It melts at 52°–53°, and at higher temperatures sublimes slowly in oily drops which soon solidify in radiating needles. By oxidation with dilute nitric acid it is converted into an acid which melts at 150°–155°. Since the orthoiodbenzoic acid obtained by Kekulé[1] from orthoiodtoluol melted at 155°–156°, our product without doubt has the same composition.

As a further proof of the constitution of orthoiodbenzylbromide we made the nitril, and from it orthoiodalphatoluic acid. To form the nitril the bromide was boiled with an alcoholic solution of potassic cyanide. The oily liquid precipitated by the addition of water was heated to 125° for four hours with fuming hydrochloric acid. When cold the oil solidified, and more of the acid separated from the solution in long needles. After removing the excess of hydrochloric acid, the crude product was purified by crystallization from hot water.

Orthoiodalphatoluic acid crystallizes in fine felted needles which are sparingly soluble in cold, readily soluble in hot water and in alcohol, ether, carbonic disulphide, and ligroin. With the limited amount of material at our disposal we were unable to raise the melting point above 95°–96°. It would seem, however, from the

[1] Berichte der deutschen chemischen Gesellschaft, **7**, 1007.

analogy of the orthobromalphatoluic acid that the melting point of our acid should be somewhat higher. When we return to this subject and have access to a larger supply of the acid, its melting point will be more carefully tested. The silver salt of this acid was made by adding argentic nitrate to an aqueous solution of the ammonium salt. It separated from the solution as a curdy precipitate which was but slightly soluble in water, readily soluble in dilute nitric acid. For analysis it was dried over sulphuric acid.

0.2615 gram of the salt gave by precipitation with HCl 0.1008 gram AgCl.

	Calculated for $C_7H_6ICOOAg$.	Found.
Ag	29.27	29.00

We also submitted the bromide to the action of alcoholic ammonia; but as the result of one experiment with a small quantity of substance we succeeded in isolating only the primary amine. The product of this reaction was treated with water, and the aqueous solution evaporated on the water-bath. Upon the addition of sodic hydrate the free base was partially precipitated as an oily liquid, and more of the oil was obtained by extracting the solution with ether. The residue left by evaporation of the ether was immediately converted into the carbonate by absorbing carbonic dioxide from the air. It was dissolved in alcohol, a little hydrochloric acid added, and the platinum salt formed by the addition of chlorplatinic acid. This salt crystallized in pale yellow microscopic prisms, which were sparingly soluble in water and cold alcohol, readily in hot, and insoluble in ether. It was purified by recrystallization from hot alcohol, washed with ether, and dried over sulphuric acid for analysis.

0.2082 gram of the salt gave on ignition 0.0468 gram platinum.

	Calculated for $(C_7H_6INH_3)_2PtCl_6$.	Found.
Pt	22.48	22.48

Since our work was interrupted by the closing of the summer term a more complete examination of the derivatives of orthoiodbenzylbromide must be reserved for another paper.

XX.—CHLORTRIBROMPROPIONIC ACID.

By Charles F. Mabery and H. C. Weber.

The formation of chlortribrompropionic acid by the action of bromine on chlorbromacrylic acid has been mentioned in a previous paper by R. Lloyd and one of us.[1] Although this reaction took place without difficulty in a chloroform solution at ordinary temperatures, the product proved to consist in great part of an oil which could not be made to crystallize. With the hope of obtaining a more satisfactory yield we tried the action of undiluted bromine at a higher temperature. Chlorbromacrylic acid, melting point 68°–70°, with a slight excess over the calculated weight of bromine, was heated to 100° for two hours in a closed tube. The excess of bromine was removed by spontaneous evaporation from the product, which was purified by pressure between folds of filter paper and crystallization from carbonic disulphide. By this method from 6.5 grams chlorbromacrylic acid we obtained 8.5 grams essentially pure chlortribrompropionic acid, or about seventy per cent. of the theoretical amount.

This acid is readily soluble in ether and alcohol, less soluble in cold than in hot carbonic disulphide and chloroform. In contact with water it forms an oil which does not solidify at 0°. From carbonic disulphide or chloroform it crystallizes by slow evaporation in oblique prisms of the triclinic system which melt at 102°–103°. In the analysis of this substance the following results were obtained:

I. 0.1582 gram of the substance gave by the method of Carius, 0.3234 gram AgCl+AgBr.

II. 0.1582 gram of the substance gave 0.3251 gram AgCl+AgBr.

III. 0.9373 gram of the substance gave 1.9049 gram AgCl+AgBr. 1.9003 gram AgCl+AgBr gave 1.1568 gram Ag.[2]

IV. 0.8096 gram of the substance gave 0.3065 gram CO_2 and 0.0631 gram H_2O.

[1] This Journal, **3**, 124; and Proceedings American Academy, **16**, 240.

[2] This determination was made with the aid of the excellent method devised by Mr. L. P. Kinnicutt. (This Journal, **4**, 22; and Proceedings American Academy, **16**, 91.)

	Calculated for $C_3H_2ClBr_3O_2$.		Found.		
		I.	II. III.		IV.
C	10.42				10.32
H	.58				.87
Cl+3Br	79.75	79.58	80.00		
Cl	10.28 } 79.75			9.62 } 79.36	
Br	69.47 }			69.74 }	

The barium, calcium and potassium salts of this acid were made and analyzed.

Baric chlortribrompropionate $Ba(C_3HClBr_3O_2)_2$.

To form the barium salt a solution of the acid was neutralized with baric carbonate and baric hydrate, filtered, and concentrated by spontaneous evaporation at the ordinary temperature. The salt crystallized in slender oblique prisms, which were quite soluble in cold water. The air-dried salt was constant when heated to 80°.

I. 0.6933 gram of the salt dried at 80° gave on ignition with H_2SO_4 0.1920 gram $BaSO_4$.

II. 0.6440 gram of the salt dried at 80° gave 0.1793 gram $BaSO_4$.

	Calculated for $Ba(C_3HClBr_3O_2)_2$.	Found.	
		I.	II.
Ba	16.59	16.26	16.37

The solubility of this salt we determined by the method of V. Meyer. A saturated solution was kept at 20° for three hours, filtered, evaporated to dryness, and the residue ignited with sulphuric acid.

I. 1.8400 gram solution gave 0.0977 gram $BaSO_4$.

II. 0.8926 gram solution gave 0.0470 gram $BaSO_4$.

These results correspond to the percentages:

I.	II.
18.82	18.66

Calcic chlortribrompropionate $Ca(C_3HClBr_3O_2)_2$.

To prepare the calcium salt we neutralized a solution of the acid with calcic carbonate and calcic hydrate, and allowed the filtered solution to evaporate spontaneously. From the concentrated solution the salt separated in clustered needles, which, when air-dried, were constant at 80°.

1.0691 gram of the salt dried at 80° gave on ignition with H_2SO_4 0.1883 gram $CaSO_4$.

	Calculated for $Ca(C_3HClBr_3O_2)_2$.	Found.
Ca	5.49	5.25

Potassic chlortribrompropionate $KC_3HClBr_3O_2.H_2O$.

The potassium salt was made by neutralizing a solution of the acid with potassic carbonate and evaporating at the ordinary temperature. This salt crystallized in rhombic prisms which are freely soluble in cold water. It contained one molecule of crystal water which was given up over sulphuric acid.

I. 1.0688 gram air-dried salt gave 0.0502 gram H_2O.

II. 1.0428 gram air-dried salt gave 0.0490 gram H_2O.

III. 0.9802 gram of the anhydrous salt gave 0.2201 gram K_2SO_4.

Calculated for $KC_3HClBr_3O_2.H_2O$.		Found. I.	II.
H_2O	4.48	4.70	4.72

Calculated for $KC_3HClBr_3O_2$.		Found. III.
K	10.20	10.08

The silver salt of this acid proved to be so unstable that we did not succeed in preparing it in a form sufficiently pure for analysis. On the addition of argentic nitrate to an aqueous solution of the acid, even in the cold it immediately became turbid from the separation of argentic chloride.

Although the barium salt is comparatively stable, we found that it was slowly decomposed when heated in aqueous solution. In order to identify the products of this decomposition, the acid was distilled with an excess of baric hydrate. The distillate was caught in bromine water, the excess of bromine allowed to evaporate, and the solution extracted with ether. The oily residue left by evaporation of the ether solidified at 0°, and possessed an odor characteristic of the substituted ethans. It would seem probable, therefore, that the volatile product of this decomposition was tribromethylen; but it was formed in such small quantity that further study was rendered extremely difficult. The residue in the retort contained baric chloride in abundance, but it gave no reaction for baric bromide. The formation of tribromacrylic acid is thus rendered extremely probable; but the residue unfortunately was lost before it could be subjected to a more critical examination. Since the summer term soon after closed, we were unable to repeat our work, and it must therefore be reserved for future study.

Chlorbromacrylic acid forms also an addition-product with hydrobromic acid. When it is heated to 100° in a closed tube with concentrated hydrobromic acid, an acid is formed which melts at 80°. Further study of this substance, which is probably chlordibrompropionic acid, will be postponed for the present.

Contributions from the Sheffield Laboratory of Yale College.

XII.—INFLUENCE OF PEPTONES AND CERTAIN INORGANIC SALTS ON THE DIASTATIC ACTION OF SALIVA.

By R. H. Chittenden and J. S. Ely.

Recent experiments[1] on the diastatic action of saliva under various conditions have revealed the fact that human mixed saliva in the presence of an equal volume of artificial gastric juice containing .05 per cent. of hydrochloric acid, is capable of forming, from a given quantity of starch, a much larger amount of sugar than the same quantity of saliva alone can do under a like degree of dilution; this being the more remarkable when it is remembered that the same percentage of acid by itself greatly retards the diastatic action. This somewhat curious fact has led us to study the individual influence of several bodies of physiological importance on salivary fermentation. It is our conviction that many of the digestive processes of the body are more dependent for their fullest action on the stimulating or other influence caused by the mere presence of many of the digestive products, than has hitherto been supposed. Experiment, to be sure, has revealed the fact that several of the products of digestion when present in the digestive mixture in excess, notably sugar in the case of salivary digestion and peptones in gastric digestion, retard the digestive process. Under ordinary circumstances, however, all conditions are favorable, in the normal body, for a rapid absorption of the digestive products, and thus any excessive accumulation is prevented. Schmidt-Mülheim[2] found in his recent study of proteid digestion, that in the case of dogs, the quantity of peptones present in the stomach was practically the same at all times during the digestion; thus 1, 4 and 6 hours after feeding a dog 61 grams of albumin, the stomach contained 3.08 grams, 3.31 grams and 2.91 grams of peptones respectively, which would seem to indicate that after the formation of a

[1] Chittenden and Griswold, this Journal, **3**, 305.

[2] Untersuchungen über die Verdauung der Eiweisskörper, Du Bois Reymond's Archiv f. Physiologie, 1879, 39.

definite quantity of the digestive products the transportation of these bodies keeps pace with the digestion. Again, there are no facts to warrant the belief that the products of one digestive process necessarily hinder the action of some other allied ferment; indeed, it is ordinarily understood that any accumulation of the digestive products simply hinders the action of that particular ferment by clogging the digestive fluid.

There is nothing inconsistent then in the statement that the products of one digestion may act as a stimulant to some other digestive process. The results of the experiments about to be described show plainly that *peptones, a product of gastric digestion, exercise a decided influence on salivary digestion, stimulating the ferment to increased action, particularly in the presence of acid which by itself completely prevents the conversion of starch into sugar.* If now we are led, in virtue of this fact, to infer that there may be a possible continuation of salivary digestion in the stomach, it follows that the ferment must act at the first period of digestion, when the acid fluids are exceedingly weak. The fact that the quantity of peptones present in the stomach at this stage of digestion may be quite small offers no objection whatever to a possible action of the peptones, since the experiments already quoted, and those about to be described, well illustrate how extremely sensitive the saliva is to a change of conditions however slight; thus even minute quantities of inorganic salts, even to the extent of only .015 per cent., exercise a decided influence on ferment action.

We may also reasonably infer that the saliva is, to a certain extent, a type of the other diastatic fluids of the body, and that the ferment itself is doubtless similar in its action to other like ferments, notably the ferment or ferments of the liver, which presumably convert the glycogen of the hepatic cells into sugar. Thus conditions which modify the diastatic action of saliva may not be wholly without similar influence on other like ferments. It has, therefore, seemed to us that the results of our work may have some bearing upon the recently published experiments of Seegen,[1] of Vienna, who found that when an aqueous solution of peptones was poured over a small piece of fresh liver, the quantity of sugar formed in a specified time was greater than in a piece of the same liver treated in a like manner but without peptones; at the same time

[1] Die Einwirkung der Leber auf Pepton, Pflüger's Archiv, **25**, 165.

however, the total amount of carbohydrate matter appeared to be increased in the presence of the peptones. Finding that the peptones themselves had no diastatic action on glycogen, Seegen then concluded that the liver possesses the power of transforming peptones into sugar and carbohydrates which are capable of being converted into sugar. While our results may in nowise affect Seegen's conclusions, they certainly suggest the possibility that the increase of sugar noticed in the presence of the peptones may be due, in part at least, to some cause other than that attributed by Seegen.

We have attempted at first in our experiments to ascertain whether by themselves or under such conditions as may presumably exist in the body, peptones have any influence on the conversion of amylaceous matter into sugar by the saliva. The amylaceous material employed was starch and glycogen, while the diastatic agent was human mixed saliva, which was usually collected in quantities of 150–250 cc. by the chewing of some tasteless substance, then filtered and thoroughly mixed before using. The saliva was ordinarily used an hour or two after collecting, and being as a rule always furnished by the same person, possessed approximately the same strength, although control experiments with starch and saliva alone under a like degree of dilution were made in each case. The method employed consisted in dissolving a weighed amount of starch or glycogen in 25 cc. of water, then adding 50 cc. of water or other fluid in which a weighed quantity of peptone or other substance was dissolved, and lastly 25 cc. of filtered saliva. The mixture, consisting of 100 cc. of fluid, was then warmed for a definite time, usually 45 minutes, at 40° C., when further action was prevented by boiling the mixture. The fluid was then diluted with water to 500 cc., and when thoroughly mixed, 50 cc. or one-tenth of the filtered fluid was precipitated by cupro-potassium tartrate, according to the method of Maercker, described in another place.[1] The copper was weighed as metallic copper, from which the percentage of reducing substance calculated as dextrose was determined by the use of Maercker's tables.

Influence of Peptones in Aqueous Solution.

The peptones employed were prepared especially for the purpose and were made as pure as possible. Three samples were prepared from thoroughly washed blood-fibrin by the action of an

[1] This Journal, **3**, 307.

active gastric juice made from a glycerin extract of pepsin and .2 per cent. hydrochloric acid, while the fourth was made from coagulated egg-albumin by the use of a similar gastric juice. All four preparations were the products of an active digestion, and were therefore free from syntonin or other preliminary products. The peptones were purified by repeated precipitation and standing under alcohol and ether, while the fourth was especially purified from soluble salts by dialysis. The following results show plainly the action of the peptones. In each experiment 1 gram of the dried peptones dissolved in 50 cc. of water was added to 1 gram of starch previously boiled with 25 cc. of water, the 25 cc. of saliva making a digestive mixture of 100 cc., in which the peptones were present to the extent of 1 per cent. In the control experiment the mixture was made up to the same volume with water. Different saliva was used in each experiment.

	Without Peptones.		*With Peptones.*	
Number of experiment.	Wt. Cu in one-tenth.	Total amount of sugar.	Wt. Cu in one-tenth.	Total amount of sugar.
1.	.0896 gram	.4557 gram	.0962 gram	.4893 gram
2.	.0911 "	.4633 "	.0974 "	.4954 "
3.	.0915 "	.4654 "	.1045 "	.5315 "
4.	.0904 "	.4598 "	.0977 "	.4969 "
5.	.0856 "	.4354 "	.0937 "	.4766 "
6.	.0835 "	.4247 "	.0949 "	.4826 "

The increased diastatic action of the saliva in the presence of the peptones is made more plainly apparent by the following table, in which are given the percentage amounts of starch converted into sugar; calling the sugar $C_6H_{12}O_6$ and the starch $C_6H_{10}O_5$.

	Without Peptones.	*With Peptones.*
1.	41.01 per cent.	44.03 per cent.
2.	41.69 "	44.58 "
3.	41.88 "	47.83 "
4.	41.38 "	44.72 "
5.	39.13 "	42.89 "
6.	38.22 "	43.43 "

It is thus seen that the presence of 1 per cent. of peptones causes an increased conversion of starch into sugar, amounting on an average to 4 per cent.

Similar experiments made with glycogen yielded like results. 2 grams of pure, dried glycogen prepared from *Pecten irradians*[1] were employed in each experiment, and the digestions continued for 30 minutes. 1 gram of peptones was used as before.

	Without Peptones.		*With Peptones.*	
	Wt. Cu in one-tenth.	Total amount of sugar.	Wt. Cu in one-tenth.	Total amount of sugar.
1.	.1405 gram	.7297 gram	.1477 gram	.7671 gram
2.	.1286 "	.6581 "	.1386 "	.7144 "
3.	.1300 "	.6653 "	.1328 "	.6771 "
4.	.1281 "	.6556 "	.1306 "	.6684 "

A few experiments were then tried, both with glycogen and starch, using 2 grams of peptones. Following are the results:

	Without Peptones. Wt. Cu in one-tenth.	*With 1 gram Peptones.* Wt. Cu in one-tenth.	*With 2 grams Peptones.* Wt. Cu in one-tenth.
Starch	.0835 gram	.0949 gram	.0960 gram
Glycogen	.1405 "	.1477 "	.1472 "
"	.1286 "	.1386 "	.1429 "
"	.1300 "	.1328 "	.1362 "

Here it is to be noticed that the presence of 2 per cent. of peptones has but little additional influence on the diastatic action. That peptones themselves were entirely free from carbohydrate matter and that the saliva is wholly without action on the peptones was clearly shown by digesting 2 grams of peptones with 25 cc. of saliva. This experiment was repeated twice, but in neither case was any reduction obtained on boiling the diluted fluid with Fehling's solution. Again, the possibility suggested itself that the peptones might exercise some influence on the precipitation of the copper, and that the increase of copper obtained when peptones were present was due not to any stimulating action they might exert on the ferment, but to a precipitation or reduction of the copper. In order to settle this point three digestions were made in the usual manner with 2 grams of glycogen. No. 1 contained, in addition, 2 grams of peptones. No. 2 had added to it after the destruction of the ferment by boiling, 2 grams of peptones, while No. 3 served as a control. A determination of the amount of sugar

[1] Chittenden, Amer. Jour. Science and Arts, **10**, 26.

in the aliquoted fluids gave the following results, clearly showing that the mere presence of the peptones has no influence on the precipitation of the copper:

No. 1. Wt. Cu in one-tenth.	No. 2. Wt. Cu in one-tenth.	No. 3. Wt. Cu in one-tenth.
.1472 gram	.1403 gram	.1405 gram

There still remained two possible chances of error, viz. the possibility of the peptones containing a trace of a diastatic ferment or of their possessing a diastatic action, and secondly that the slightly acid reaction of the peptone solutions might exert some modifying influence. The former supposition was easily disproved by making a digestion of starch and peptones alone. This led, as would naturally be expected, to a negative result; the solution showing no reducing action whatever. An endeavor was then made to obtain the same result in a somewhat different manner: a series of digestions was made, in which one of the peptone solutions was vigorously boiled before being added to the starch solution, the digestions then being made in the usual manner.

	Without Peptones. Wt. Cu in one-tenth.	*With 1 gram Peptones.* Wt. Cu in one-tenth.	*Peptone sol. boiled.* Wt. Cu in one-tenth.	*Peptone sol. boiled and water replaced.* Wt. Cu in one-tenth.
No. 1.	.0856 gram	.0937 gram	.0950 gram	.0952 gram
No. 2.	.0904 "	.0977 "	.1035 "	...

That the peptones contain no ferment is plainly apparent, but the slight increase of sugar when the peptone solution is boiled is certainly somewhat singular. Three of the peptones employed in these experiments gave, when dissolved in water, very faintly acid solutions. The acidity of 1 gram of peptones, however, was never sufficient to neutralize the alkali of 25 cc. of saliva.[1] The fourth sample, which was purified by dialysis, gave a neutral solution, and this sample did not differ in its action in the least from the other three. An attempt was made, however, to neutralize one of the peptone solutions, previous to the digestion, by the use of an exceedingly dilute alkali. The following results were obtained:

[1] Neutral saliva appears to have as great a diastatic action as saliva of normal alkalinity. Thus while a digestion made with freshly collected alkaline saliva gave .0905 gram Cu, a portion of the same saliva neutralized gave .0943 gram Cu under the same conditions.

Without Peptones.	*With 1 gram Peptones.*	*With 1 gram neutralized Peptones.*
Wt. Cu in one-tenth.	Wt. Cu in one-tenth.	Wt. Cu in one-tenth.
.0915 gram	.1045 gram	.0991 gram

The slight decrease of copper in the neutralized peptone, as later experiments would seem to indicate, is due probably to the retarding influence of the alkali salt formed by neutralization, although it seems hardly possible that such a minute trace could exert any influence whatever on the action of the saliva.

O. Nasse[1] in his work on unformed ferments, found that in 4 per cent. solutions of certain inorganic salts there was an increased ferment action. It therefore seemed desirable to ascertain in the present case whether the inorganic salts contained in the peptones could exert any influence on the salivary ferment. The four samples of peptones contained the following percentages of ash:

No. 1.	No. 2.	No. 3.	No. 4.
1.71 per cent.	0.89 per cent.	1.25 per cent.	1.58 per cent.

With the exception of No. 4, the ash was composed of sodium chloride, sodium phosphate and calcium phosphate.

No. 4, which was prepared from coagulated albumin and purified by dialysis, left an ash composed wholly of calcium phosphate. The following results show the individual influence of the three inorganic salts on the diastatic action of saliva when present in the digestive fluid in approximately such percentages as the peptones give when added to the starch and saliva mixture:

First Experiment.

		Wt. Cu in one-tenth.
Saliva and starch alone,		.0872 gram
" "	+.012 gram NaCl = .012 per cent.	.0862 "
" "	+.024 " " = .024 "	.0925 "
" "	+.012 " Na_2HPO_4 = .012 per ct.	.0886 "
" "	+.024 " " = .024 "	.0834 "

Second Experiment.

		Wt. Cu in one-tenth.
Saliva and starch alone,		.0844 gram
" "	+.015 gram $CaHPO_4$ = .015 per cent.	.0839 "
" "	+.030 " " = .030 "	.0870 "

[1] Untersuchungen über die ungeformten Fermenten, Pflüger's Archiv, **11**, 138.

From these results it is apparent that no one of the inorganic salts of the peptones is present in sufficient quantity to have any stimulating action whatever in aqueous solution, for increased diastatic action is noticed only in the presence of 24 milligrams of sodium chloride, an amount much larger than the total ash of 1 gram of peptones. Again, peptone No. 4, which was freed from all trace of chloride by dialysis, had exactly the same stimulating effect as the other samples.

In order to ascertain exactly what the influence of the *mixture* of inorganic salts, as present in the peptones, would be, a series of digestions was made, in two of which the ash of 1 gram and of 2 grams of peptones respectively were employed; the ash, as in the experiments with the peptones themselves, being dissolved in 50 cc. of water, and in this manner added to the starch solution previous to the addition of the 25 cc. of saliva. The peptones employed were the ones which contained 1.71 per cent. of ash; thus the digestive mixtures contained respectively .017 and .034 per cent. of inorganic matter. The following results were obtained:

Saliva and Starch alone.	*With Ash from 1 gram Peptones.*	*With Ash from 2 grams of Peptones.*
Wt. Cu in one-tenth.	Wt. Cu in one-tenth.	Wt. Cu in one-tenth.
.0862 gram	.0851 gram	.0715 gram

It is thus very apparent that the stimulating action of the peptones is not due to the inorganic salts contained in them, for these latter, as the foregoing experiment shows, have, by themselves, in aqueous solution, a retarding influence. We therefore deem it proven that peptones under such conditions as have already been described have in aqueous solution a stimulating influence on salivary digestion. In other words, peptones when present to the extent of 1–2 per cent. cause, under the same conditions as saliva alone, an increased conversion of starch into sugar amounting on an average to 4 per cent.

Influence of Peptones in Acid Solution.

Previous experiments[1] have plainly demonstrated the extreme sensitiveness of the saliva to the action of dilute acids. Thus the addition of 50 cc. of .05 per cent. hydrochloric acid to a digestive

[1] Chittenden and Griswold, this Journal, **3**, 313.

mixture, thereby making the fluid contain but .025 per cent. of acid, very greatly diminishes the diastatic action. This result has been recently verified by J. N. Langley,[1] as also the results of Chittenden and Griswold in regard to the destruction of the salivary ferment by gastric juice and by .2 per cent. hydrochloric acid at 40°C.

An attempt was now made to ascertain the influence of peptones in an acid solution of the above strength, viz. .025 per cent. The experiments were conducted in the same manner as the preceding, with this exception: the peptones, instead of being dissolved in water, were in each case dissolved in 50 cc. of .05 per cent. hydrochloric acid. 1 gram of peptones was used in each experiment, starch being the amylaceous material employed.

	Saliva alone.		*Saliva and Acid.*		*Saliva, Acid and Peptones.*	
	Wt. Cu in one-tenth.	Total amount of sugar.	Wt. Cu in one-tenth.	Total amount of sugar.	Wt. Cu in one-tenth.	Total amount of sugar.
1.	.0896 gram	.4557 gram	.0076 gram	.0389 gram	.1068 gram	.5428 gram
2.	.0911 "	.4633 "	.0079 "	.0405 "	.1070 "	.5439 "
3.	.0915 "	.4654 "	.0098 "	.0502 "	.1060 "	.5388 "
4.	.0835 "	.4247 "	...	...	.0985 "	.5010 "

The percentage amounts of starch converted into sugar under the three conditions are as follows:

	Saliva alone.	*Saliva and Acid.*	*Saliva, Acid and Peptones.*
1.	41.01 per cent.	3.50 per cent.	48.85 per cent.
2.	41.69 "	3.64 "	48.95 "
3.	41.88 "	4.51 "	48.48 "
4.	38.22 "	...	45.09 "

Similar experiments were tried with glycogen, 2 grams of this substance being dissolved in 25 cc. of water and employed in the same manner as the starch; 1 gram of peptones was used as before. The following results were obtained:

	Saliva alone. Wt. Cu in one-tenth.	*Saliva and Acid.* Wt. Cu in one-tenth.	*Saliva, Acid and Peptones.* Wt. Cu in one-tenth.
1.	.1300 gram	.0049 gram	.1408 gram
2.	.1281 "	trace	.1424 "

[1] Foster's Journal of Physiology, 3, 246.

It is thus seen that the presence of 1 gram of peptones exercises a very remarkable influence on the diastatic action of saliva in an acid solution of the above strength. The peptones are present in the digestive mixture to the extent of only 1 per cent., while the acid is but .025 per cent., yet this quantity of peptones is sufficient not only to counteract the retarding influence of the acid, but increases the conversion of the starch to the extent of 7 per cent. above the action of the saliva alone. Increasing the amount of peptones to 2 per cent. does not appear to have any effect whatever, as the following results show:

	1 gram Peptones and .025 per cent. Acid. Wt. Cu in one-tenth.	*2 grams Peptones and .025 per cent. Acid.* Wt. Cu in one-tenth.
1.	.1060 gram	.1084 gram
2.	.0985 "	.0974 "

In acid solutions of increased strength the peptones appear to exercise but slight if any influence; thus when the solution contained .1 per cent. hydrochloric acid, no diastatic action at all was observed, even in the presence of the peptones. In .05 per cent. acid solution however, one-tenth of the diluted and mixed digestive fluid yielded .013 gram Cu, showing a slightly increased action over and above what the acid fluid alone would give.

Control experiments with saliva, peptones and acid without starch yielded negative results, thus showing that the saliva is entirely without action on the peptones in an acid solution of the above strength. Again, digestions of starch, peptones and acid without saliva also gave negative results, proving that the peptones are wholly without diastatic action in the acid fluid. We deemed it advisable next to examine how far inorganic salts could influence the action of the ferment in an acid solution of the strength used. In aqueous solution it will be remembered the inorganic salts experimented with had but little or no action. In the acid solution the salts used were the same as before, viz. those present in the ash of the peptones. The experiments were conducted in the same manner as the preceding; 100 cc. being the volume of the mixed fluid, of which 25 cc. were filtered saliva, 25 cc. water containing 1 gram of starch and 50 cc. .05 per cent. hydrochloric acid containing the salt.

FIRST EXPERIMENT.

	Wt. Cu in one-tenth.
Saliva and starch alone,	.0872 gram
" " +.05 per cent. HCl = .025 per cent.	.0088 "
" " " " " +.012 gram NaCl	.0132 "
" " " " " +.012 gram Na_2HPO_4	.0120 "

SECOND EXPERIMENT.

	Wt. Cu in one-tenth.
Saliva and starch alone,	.0835 gram
" " +.05 per cent. HCl = .025 per cent.	.0050 "
Saliva and starch+.05 per cent. HCl+.012 gram $CaHPO_4$	.0079 "
Saliva and starch+.05 per cent. HCl+.015 gram $CaHPO_4$	.0490 "
Saliva and starch+.05 per cent. HCl+.024 gram $CaHPO_4$	.0600 "

It is thus evident that sodium chloride and phosphate when present to the extent of .012 per cent. exercise but a very slight influence on the action of the saliva. Calcium phosphate, however, is seen to decidedly increase the diastatic action, though the amount contained in the peptones can have but little influence on the formation of sugar. Very striking is the great increase of sugar formed in the presence of 24 milligrams of calcium phosphate. This result is certainly suggestive of a possible utility of the calcium phosphate invariably present in wheat, oats and carbohydrate matter in general. What the exact explanation of the action of the phosphate in such a weak acid solution is, is of course hypothetical. The salt dissolves, in part at least, in the acid, and is thus probably modified with formation of bodies more favorable to the action of the ferment; it certainly cannot diminish to any extent the strength of the acid.

The influence of the combined inorganic matter of the peptones was now determined by experiment with the ash of No. 1, which contained 1.71 per cent.

Saliva and Starch. +.05 per cent. HCl. +1 gram Peptone. +Ash 1 gram Peptone.

	Wt. Cu in one-tenth.	Wt. Cu in one-tenth.	Wt. Cu in one-tenth.	Wt. Cu in one-tenth.
1.	.0866 gram	.0053 gram	.1058 gram	.0370 gram
2.	.0862 "	...	...	.0123 "

Thus, in the sample containing the largest percentage of ash, and presumably therefore of calcium phosphate, and under the same conditions as this salt appears to work to the best advantage, only a slight increase is noticed in the diastatic action of the saliva. It is therefore evident that while the addition of 50 cc. .05 per cent. hydrochloric acid to an equal volume of saliva and water brings the diastatic action down almost to zero, the addition of 1 gram of peptones to this acid fluid increases the diastatic action of the saliva to above its normal amount. In other words, the presence of 1 per cent. of gastric peptones in a salivary mixture containing .025 per cent. of acid acts as a stimulant to the diastatic ferment, causing it to act with greatly increased vigor. This fact appears to us to be of prime importance in solving the question as to the possibility of a continued action of the salivary ferment in the stomach. In 1881 one[1] of us, experimenting with human saliva, found that its diastatic action was increased by the presence of very minute quantities of hydrochloric acid; thus, while the quantity of sugar formed by freshly collected saliva was regarded as 100, the quantity formed by saliva of the same collecting in a mixture containing .005 per cent. of hydrochloric acid was 110. Increasing the percentage of acid diminishes the diastatic action, until at last, when the fluid contains .025 per cent. of hydrochloric acid, the formation of sugar is almost entirely stopped. Again, it was found[2] on digesting 25 cc. of human saliva with 50 cc. of gastric juice containing .2 per cent. of hydrochloric acid, at 40°C. for two hours, that the diastatic ferment was entirely destroyed; likewise that simple warming of the saliva with .2 per cent. acid at 40°C. for two hours was sufficient to destroy the greater part of the ferment, as was evinced by the low diastatic power of the neutralized fluid. Both of these results have received recent confirmation from the experiments of J. N. Langley[3] on the diastatic ferment of the parotid of rabbits. From his experiments he concludes that the ptyalin is destroyed by .2–.04 per cent. hydrochloric acid in from 7 to 24 hours at 40°C., and that the presence of .014 per cent. of acid is sufficient to destroy all but the merest trace of ferment in five minutes at 39°C. It appears to us, however, that in the case of human saliva at least there may be in the presence of a very dilute acid a simple stopping of the diastatic action without destruction of the ferment; thus, in the presence of

[1] Chittenden and Griswold, this Journal, **3**, 305. [2] Chittenden and Griswold, *loc. cit.*
[3] Foster's Journal of Physiology, **3**, 246.

.025 per cent. of acid there is but little diastatic action, but if that percentage of acid is sufficient to destroy the ferment in such a short time, in what manner does the 1 per cent. of peptones in an acid solution of the same strength cause such an increased formation of sugar? Again, the experiments of Chittenden and Griswold showed that by warming a mixture of starch, saliva and artificial gastric juice of weak acidity, at 40°C. for 45 minutes, the diastatic action of the saliva was greatly increased; thus, in the digestion of 1 gram of starch + 25 cc. of water + 50 cc. of gastric juice, containing .05 per cent. hydrochloric acid + 25 cc. saliva, the amount of sugar formed as compared with the amount found by the saliva alone was 133 : 100; while, as the present experiments show, the presence of .025 per cent. hydrochloric acid alone stops the action almost completely. It therefore seems probable that in the presence of such dilute acids as the above the ferment is simply hindered in its action, the presence of the peptones being sufficient to counteract the retarding influence of the acid. That this view as to the non-destruction of the ferment is correct, as regards human saliva at least, we think is plainly demonstrated by the following experiment. 75 cc. of filtered saliva were divided into three equal parts, which were treated as follows:

1st. 25 cc. saliva + 25 cc. .05 per cent. HCl warmed at 40°C. for 45 minutes. Solution then neutralized with Na_2CO_3. 1 gram of starch made into a paste with 50 cc. H_2O was then added and the mixture warmed at 40°C. for 45 minutes. Solution boiled and diluted to 500 cc. 50 cc. of this solution reduced .0862 gram Cu.

2d. 25 cc. saliva + 25 cc. H_2O + 50 cc. .05 per cent. HCl warmed at 40°C. for 45 minutes. Solution then neutralized with Na_2CO_3. 1 gram starch made into a paste with 25 cc. H_2O was then added and the mixture warmed at 40°C. for 45 minutes. Solution boiled and diluted to 500 cc. 50 cc. of this solution reduced .0805 gram Cu.

3d. 25 cc. saliva + 75 cc. H_2O warmed at 40°C. for 45 minutes. 1 gram of starch made into a paste with 25 cc. H_2O was then added and the mixture warmed at 40°C. for 45 minutes. Solution boiled and diluted to 500 cc. 50 cc. of this solution reduced .0824 gram Cu.

Here it is plainly seen that the ferment has not been in the least affected by the action of .025 per cent.[1] hydrochloric acid at this

[1] It should be mentioned here that the real percentage of acid is somewhat less than .025, owing to the slight alkalinity of the saliva. Ordinarily, however, the alkalinity is not so great in a sample of several hundred cubic centimeters as in a small quantity of freshly-secreted saliva. That there might be no possible chance of error, 25 cc. of mixed saliva were carefully neutral-

temperature. In the case of .1 or .2 per cent. acid the peptones are wholly without influence, since these strengths of acid are capable of destroying the ferment. It is evident that the salivary ferment is ultimately destroyed in the stomach by the gastric juice, but this fact does not necessarily preclude the possibility of a continued action of the saliva in the stomach. There is a growing impression that in the first stage of stomach digestion there is but little or no free acid present; thus Reinhard v. d. Velden[1] claims, as a result of observation, that for the first three-fourths of an hour after eating a hearty meal, human gastric juice fails to contain much if any free acid. It now seemed desirable to ascertain the rapidity with with starch is converted into sugar by the saliva. 125 cc. of filtered saliva were thoroughly mixed, and 12 cc. of this fluid were used in each experiment. The starchy solution was made by boiling .5 gram starch with 40 cc. of water, and to this solution the 12 cc. of saliva were added, making approximately 52 cc. of fluid. The mixtures were kept at a temperature of 40°C. for the specified time, then boiled to destroy the ferment. Each fluid was then diluted to 200 cc. and the sugar determined as before in 50 cc. of the mixed and filtered solution. Following are the results:

Period of digestion.	Wt. Cu in one-fourth.	Total amount sugar.	Percentage of starch converted into sugar.
1 minute	.0870 gram	.4425 gram	39.82 per cent.
5 minutes	.0963 "	.4898 "	44.09 "
10 "	.0991 "	.5040 "	45.36 "
15 "	.1005 "	.5111 "	45.99 "
30 "	.1040 "	.5286 "	47.57 "
45 "	.1087 "	.5525 "	49.72 "
1 hour	.1109 "	.5637 "	50.73 "
2 hours	.1147 "	.5842 "	52.57 "

This experiment makes it very apparent that by far the greater part of the starch is almost immediately converted into sugar. It seems therefore quite possible, especially in view of the action of peptones in a weak acid solution, that in the case of human beings

ized with diluted hydrochloric acid. Then 25 cc. of .05 per cent. HCl were added, making an exactly .025 per cent. HCl solution. This mixture was then warmed at 40°C. for 45 minutes, after which it was exactly neutralized with Na_2CO_3 solution. One gram of starch in 50 cc. H_2O was then added and the whole warmed at 40°C. for 45 minutes; 50 cc. or one-tenth of the diluted fluid yielded .0882 gram Cu. Thus here, as in the above experiments, it is plainly evident, from the diastatic action of the neutralized saliva, that the ptyalin is not destroyed nor even affected by .025 per cent. of actual HCl under the above conditions.

[1] Zeitschrift f. physiolog. Chem. 3, 205.

there may be a continuation of salivary digestion in the stomach, provided the contents of the stomach during the first stage of digestion do not contain more than .025 per cent. of free acid.

Influence of Peptones in Alkaline Solution.

Previous experiments have demonstrated that the addition of sodium carbonate to saliva has a retarding influence on salivary digestion. It now seemed advisable to study the influence of peptones in the presence of dilute solutions of sodium carbonate, with especial reference to the pancreatic ptyalin, for presumably in the intestinal canal the diastatic ferment there present acts on starch in an alkaline medium. .6 per cent., .3 per cent. and .1 per cent. solutions of sodium carbonate were employed, experiments being tried with both starch and glycogen. 1 gram of peptones was used in each case, and as this amount was dissolved in 50 cc. of the dilute alkali, the digestive mixture of 100 cc. contained approximately one-half the percentage of alkali employed. The following results were obtained:

1. With .6 per cent. Na_2CO_3 and 1 gram peptones.

	Saliva alone. Wt. Cu in one-tenth.	*Saliva* + 50 *cc. Alkali.* Wt. Cu in one-tenth.	*Saliva, Alkali and Peptones.* Wt. Cu in one-tenth.
Starch	.0905 gram	.0239 gram	.0456 gram
"	.0904 "	.0222 "	.0486 "
"	.0835 "	.0214 "	.0515 "
Glycogen	.1300 "	.0312 "	.0683 "

2. With .3 per cent. Na_2CO_3 and 1 gram peptones.

	Saliva alone. Wt. Cu in one-tenth.	*Saliva* + 50 *cc. Alkali.* Wt. Cu in one-tenth.	*Saliva, Alkali and Peptones.* Wt. Cu in one-tenth.
Starch	.0904 gram	.0393 gram	.0685 gram
"	.0835 "	.0331 "	.0710 "
Glycogen	.1281 "	.0423 "	.1050 "

3. With .1 per cent. Na_2CO_3 and 1 gram peptones.

	Saliva alone. Wt. Cu in one-tenth.	*Saliva* + 50 *cc. Alkali.* Wt. Cu in one-tenth.	*Saliva, Alkali and Peptones.* Wt. Cu in one-tenth.
Glycogen	.1281 gram	.0908 gram	.1197 gram

It becomes evident then from these experiments that in a solution containing either .3 per cent. or .15 per cent. of sodium carbonate, the presence of the peptones nearly doubles (quite and even more in the case of glycogen) the diastatic action, bringing it up almost to the action of the unaltered saliva. It may be questionable whether these experiments afford proof positive that the peptones stimulate the pancreatic ferment in the conversion of starch into sugar in the intestinal canal, but it is certainly proven that under such conditions as have been described here, the presence of 1 per cent. of peptones in a .3 per cent. sodium carbonate solution causes a greatly increased formation of sugar. Thus it seems probable that in the proteid and diastatic pancreatic digestion the formation of peptones, which must go on side by side with the formation of sugar, affords a decided aid to the latter process.

We next endeavored to ascertain whether the salts already experimented with have any influence on diastatic action in alkaline solutions of the strength specified. The following experiments were tried:

FIRST EXPERIMENT.

	Wt. Cu in one-tenth.
Saliva and starch alone,	.0872 gram
" " +50 cc. .6 per cent. Na_2CO_3=.3 per cent. alkali	.0220 "
" " " " +.012 gram NaCl	.0287 "
" " " " +.012 " Na_2HPO_4	.0275 "

SECOND EXPERIMENT.

	Wt. Cu in one-tenth.
Saliva and starch alone,	.0844 gram
" " +50 cc. .6 per cent. Na_2CO_3=.3 per cent. alkali	.0225 "
" " " " +.015 gram $CaHPO_4$	.0211 "
" " +50 cc. .3 per ct. Na_2CO_3=.15 per cent. alkali	.0348 "
" " " " +.015 gram $CaHPO_4$	.0395 "

It is thus very evident that these salts have little or no influence on diastatic action, in alkaline solutions of the strength used. It next remained to try the influence of the ash of the peptones in alkaline solution. The ash of 1 gram of peptones was employed, the experiment being conducted in the same manner as the preceding. The peptones used were those with 1.71 per cent. of ash. Following are the results:

	Wt. Cu in one-tenth.
Saliva and starch alone,	.0862 gram
" " +50 cc. .6 per cent. Na_2CO_3=.3 per cent. alkali	.0216 "
" " " " +ash 1 gram peptone	.0313 "
" " " " +1 gram peptone	.0520 "

Saliva and starch alone,			.0862 gram
" "	+50 cc. .3 per cent. Na_2CO_3=.15 per cent. alkali		.0305 "
" "	"	+ash 1 gram peptones	.0400 "
" "	"	+1 gram peptone	.0740 "

We therefore deem it safe to conclude that the inorganic salts contained in the peptones play but an unimportant part in the stimulating action noticed in an alkaline solution of the strength specified.

MARCH 20, 1882.

ON THE DETERMINATION OF REVERTED PHOSPHATES.[1]

BY THOMAS S. GLADDING.

In an investigation on the subject of reverted phosphoric acid, the first question that arises is, What is meant by this term? The curious phenomenon of a decrease in the amount of soluble phosphate in a superphosphate and its reversion into a form insoluble in water, but soluble in the organic salts of ammonia, in weak acids and other reagents, has been attributed to several different causes.

According to the most common explanation[2] it is due to the gradual interaction between the soluble or monocalcic phosphate formed in the manufacture, and the still undecomposed tricalcic phosphate of the original rock, this reaction resulting in the formation of the intermediate compound dicalcic phosphate.

Again, it has been noticed that this reversion is especially large when the amounts of iron and alumina present are considerable, and in such cases it has been attributed[3] to the formation of phosphates of iron and alumina having the solvent properties specified above.

Again, from experiments in our own laboratory it has been found that this reversion is very noticeable in acid phosphates, which, after treatment with sulphuric acid, have been mixed with natural phosphates containing large amounts of carbonate of lime. The reac-

[1] Read before the American Chemical Society, March 17, 1882.

[2] Zeit. für analyt. Chem. **10**, Fresenius. [3] Zeit. für analyt. Chem. **19**, Z. Meyer.

tion that takes place between the monocalcic phosphate and carbonate of lime probably results in the formation of either the dicalcic or tricalcic phosphate. This latter salt, though insoluble in water, is readily taken up, on account of its fine state of division, by the reagents used for the estimation of reverted phosphates.

From these different explanations of the character of reverted phosphate it is evident that the term is not capable of a strict chemical definition. It may consist in any given case of one or of several chemical compounds. The best definition that can be given is the general one condensed into the name itself. Reverted phosphates are those which, originally insoluble, but having been made soluble, have reverted or returned to the insoluble condition. They must now, however, be looked upon as:

(1) Just over the border line that separates the soluble from the insoluble, lying very close to the soluble and being brought back by a slight addition to the solvent power of water; and, as

(2) Widely separated and different in solubility from the insoluble form which they originally possessed. Like the flats lying just above the river's edge, they must be wholly covered by a slight rise in the water that affects the banks but little.

The object of the inquiry here described has been to establish the above distinctions, and to find a method of separation that shall in the actual analysis recognise them as nearly as possible. The course pursued has been that followed in similar inquiries:

I. An examination of the solubility of the different natural phosphates used in the manufacture of superphosphates.

II. An examination of the solubility of the different chemical compounds of which reverted phosphates have been found to consist; and

III. An attempt based upon the results of these two inquiries to find the best method of separating these two classes.

In the examination of the natural phosphates, five different forms were taken as typical of all. These were:

1. *Apatite*, as type of the nearly pure tricalcic form in its most insoluble condition.

2. *South Carolina rock*, containing besides tricalcic phosphate, phosphates of iron and alumina, and carbonate of lime.

3. *Bone Ash*, the great organic source of phosphate.

4. *Navassa rock*, typical on account of its large percentage of iron and alumina; and finally,

5. *Curaçao phosphate*, as type of the island phosphates, notable for their peculiar mechanical condition and greater solubility in the organic salts of ammonia.

In examining the solubility of these natural phosphates, attention was first given to the effect of different relative proportions of phosphate and solvent. The standard method of Fresenius, Luck and Neubauer[1] was followed, using 50 cc. of citrate of ammonia solution, of sp. gr. 1.09, and made as nearly neutral as possible, time 30 minutes, temp. 35° C. Two series of experiments were made. In the first, one gram of substance was taken; in the second, $\frac{1}{10}$ of a gram.

	SERIES I.	SERIES II.
	P_2O_5 dissolved.	P_2O_5 dissolved.
Apatite	0.40 per cent.	1.54 per cent.
South Carolina rock	2.00 "	6.60 "
Bone Ash	2.60 "	8.30 "
Navassa	2.65 "	10.10 "
Curaçao	4.40 "	16.00 "

Comparing these tables, we see at once the fact that has been commented upon very frequently of late by German chemists as regards superphosphates, and to which special attention has been called within a few months by a printed letter of Dr. S. W. Johnson, in the case of Curaçao phosphate, namely, that the percentage of phosphate dissolved increases very largely with the increase of solvent, or, what is the same, the decrease of substance taken for analysis. These tables show that this is true not only of reverted phosphates as found by the former, nor of Curaçao phosphate as shown by the latter, but also of all natural phosphates, including even the difficultly soluble apatite. This fact has a very important bearing upon the error involved in the determination of reverted phosphoric acid by this method, *i. e.* an error as regards the strict separation of the reverted phosphates from the insoluble phosphates. Thus, supposing five superphosphates after the extraction of the soluble to contain no reverted phosphate, but to contain 10 per cent. of the above raw phosphates respectively, corresponding to about 3 per cent. of insoluble phosphoric acid, the citrate would attack these raw phosphates, and instead of the error being

[1] Zeit. für analyt. Chem. **10.**

0.04, 0.20, 0.26, 0.26 and 0.44 per cent. as would naturally be supposed from Series I., it would in reality be 0.15, 0.66, 0.83, 1.01 and 1.60 per cent. as shown by Series II. Thus, the superphosphates would be reported as containing these latter amounts of reverted phosphoric acid, when in fact they contained none whatever.

This same fact of increased solvent power obtained by increasing the amount of solvent salt was shown to be true also of oxalate of ammonia, by treating 2 grams of Navassa rock and Curaçao phosphate with 1, 5, and 10 grams of the salt dissolved in 100 cc. of water, at a temperature of 100° C. for 30 minutes.

SERIES III.

	1 gram.	5 grams.	10 grams.
Navassa, P_2O_5 dis.,	2.20	8.75	12.15
Curaçao, " "	2.50	12.30	17.60

The influence of increase of temperature upon the amount of rock dissolved was shown by treating one gram of the different phosphates with 100 cc. of water containing four grams of oxalate at 20°C. and at 100°C.

SERIES IV.

	Apatite.	So. Car. Rock.	Bone Ash.	Navassa.	Curaçao.
At 20°C. P_2O_5 dis.	0.36 per ct.	2.25 per ct.	2.72 per ct.	2.85 per ct.	5.51 per ct.
" 100° " "	2.16 "	5.80 "	8.78 "	9.40 "	15.30 "

In performing the above experiments at 100°C. a strong odor of evolved ammonia was observed, and it was also found that the filtrates were decidedly acid in reaction. The importance of this and its bearing upon the subject will be better seen further on.

The results thus far given show very clearly the cause of much of the confusion that has arisen over the determination of reverted phosphates. This lies in the great facility with which the citrate and oxalate solutions attack the insoluble phosphate, especially when the proportion of solvent is increased or when the temperature of digestion is raised. Many chemists have been led by these difficulties to seek a better method. The suggestion has frequently been made that a weak or dilute acid be employed as a substitute for the organic salts of ammonia. Thus Grupe and Tollens[1] recom-

[1] Berichte der deutsch. chem. Gesellschaft, **14**, 754.

mend the use of a ½ per cent. citric acid solution. The solvent power of this acid of ½ per cent., also of oxalic acid of ½ per cent. and $\frac{1}{10}$ per cent., also of hydrochloric acid of $\frac{1}{100}$ normal strength, upon the natural phosphates was examined. 100 cc. of each of the above solvents were taken, the temperature of digestion was 40°C., time one hour. One gram was taken with each acid, and in addition also $\frac{1}{10}$ of a gram with the citric acid of ½ per cent.

SERIES V.

Acid employed—		Citric ½ per ct. 1 gram.	Citric ½ per ct. $\frac{1}{10}$ gram.	Oxalic ½ per ct. 1 gram.	Oxalic $\frac{1}{10}$ per ct. 1 gram.	HCl $\frac{1}{100}$ normal. 1 gram.
Apatite,	P_2O_5 dis.	0.74 per ct.	2.70 per ct.	3.20 per ct.	1.08 per ct.	2.56 per ct.
So. Car. rock,	"	2.80 "	11.40 "	8.75 "	2.68 "	4.25 "
Bone Ash,	"	3.80 "	11.80 "	9.23 "	4.15 "	3.85 "
Navassa,	"	3.30 "	14.00 "	9.96 "	3.50 "	4.15 "
Curaçao,	"	4.20 "	19.80 "	9.12 "	4.00 "	3.35 "

Supposing a fertilizer to contain 10 per cent. of insoluble rock, the citric acid would make the reverted phosphoric acid 0.27 per cent., 1.14 per cent., 1.18 per cent., 1.40 per cent., 1.98 per cent. respectively in excess of the actual amount present. The excess thus introduced would be considerably greater than that caused by the solvent action of the citrate of ammonia solution, *vide* Series II., and the claim made for the citric acid solution by Grupe and Tollens that it dissolves nearly the same amount of phosphate from different quantities of substance taken for analysis shown to be wholly unfounded as regards its action on raw phosphates. (Compare columns 1 and 2 above.)

The action of the different solvents upon the dicalcic and tricalcic salts was next studied. These salts were obtained by precipitation, and on analysis found to agree so closely with the theoretical composition as to show the admixture of traces only of other forms. After thorough washing they were mixed with about an equal weight of calcium sulphate, in order to imitate the conditions under which they are found in a superphosphate. These mixtures were then thoroughly air-dried. One gram of each was now treated with the different solvents, already employed, for 30 minutes at a temperature of 40°C. The mixture of the dicalcic salt contained 19.20 per cent. of P_2O_5, of the tricalcic salt 13.00 per cent.

SERIES VI.

Solvent.	$2CaOP_2O_5$.	$3CaOP_2O_5$.
160 cc. ¼ per cent. citric acid, P_2O_5 dis. =	{ 10.60 / 9.31 per cent.	10.26 per cent.
100 cc. $\frac{1}{10}$ " oxalic acid, "	5.32 "	5.10 "
" 1 normal HCl " "	3.42 "	1.90 "
50 cc. cit. of ammonia sol. "	19.20 "	13.00 "
50 cc. H_2O+1 gram oxal. ammo. "	{ 19.00 / 19.05 "	11.50 "

It will be seen from this table that the citrate solution dissolves both forms perfectly; that the citric acid, though fairly successful with the tricalcic salt, dissolves only one-half of the dicalcic salt; that the other acids, notably the mineral acid HCl, fall far below the citric in this respect. Special attention is called to the vigor of the weak solution of oxalate of ammonia. Though only one gram is used, it dissolves all but a trace of the dicalcic salt, and falls but little short of dissolving all the tricalcic form. In the original article of Fresenius, Luck and Neubauer, the weak acids were discarded an account of their inability to take up the reverted phosphate. This conclusion is corroborated by these experiments, with the additional objection proved by Series V., namely, the greater extent to which they dissolve the insoluble phosphate. They found also that oxalate of ammonia solution dissolved the dicalcic phosphate equally with the citrate salt, but abandoned its use on account of the vigor with which it attacked the raw phosphates. But they employed in their published experiments a very large amount of oxalate, six grams of the salt being taken. But it is here found that a much weaker solution of the oxalate is effective for dissolving the dicalcic salt. As to its solvent action upon the natural phosphates, a series of experiments proved that it was not as energetic in this respect as the citrate of ammonia solution, dissolving considerably less than the latter. On account of the many advantages possessed by an oxalate of ammonia solution over the citrate solution (1) as regards ease of preparing a perfectly uniform, neutral solution, (2) as to the greater facility of filtering and washing, and many others, many chemists urged and secured its adoption at the Cincinnati convention of agricultural chemists of 1881. But further experiments, to be described later, reluctantly compelled the conclusion that it cannot supersede the citrate of ammonia solution.

A series of experiments were now made upon a sample of acid phosphate, in order to compare the results obtained by the different methods, and to throw light, if possible, upon the causes of discrepancy. A sample made from Navassa rock was chosen on account of the large amount of reverted phosphate usually present in this class of fertilizers. The total phosphoric acid in the sample was 17.00 per cent., the soluble was 5.00 per cent., leaving 12.00 per cent. of reverted and insoluble. After thoroughly washing out the soluble, one gram was treated with 50 cc. of citrate of ammonia solution, and the directions of Fresenius carefully followed. Another gram was treated in exactly the same way, using however as a solvent 50 cc. of water containing in solution one gram of oxalate of ammonia. The following results were obtained:

SERIES VII.

	P_2O_5 dissolved.	P_2O_5 undissolved.
By citrate solution or "Washington method,"	6.10 per cent.	5.90 per cent.
By oxalate solution,	6.15 "	5.85 "

These two methods give results that are gratifying as regards their agreement. Subsequent experiments, however, showed conclusively that both were far from the truth.

Two grams of the same sample were now, after the extraction of the soluble phosphate, treated according to the method adopted by the agricultural chemists at Cincinnati, known as the "Cincinnati method." The two grams of residue were washed from the filter paper into a beaker with 100 cc. of water, containing in solution two grams of oxalate of ammonia. (This is the same amount of oxalate in proportion to the quantity of substance taken as is used in the above determination.) 400 cc. of water are brought to boiling, and the beaker closely covered now introduced in the boiling water, the lamp being at the same time removed. The temperature of the liquid in the beaker will rise to about 70° C. in a few minutes, and will then slowly sink during an hour to about 40° C. The beaker is briskly rotated at intervals. Two grams were treated in exactly the same manner, using, however, instead of the oxalate solution 100 cc. of the citrate solution.

SERIES VIII.

	P_2O_5 dissolved.	P_2O_5 undissolved.
By oxalate of ammonia	8.55 per cent.	3.45 per cent.
" citrate "	9.85 "	2.15 "

The point of interest connected with these results is the much larger amount of phosphoric acid dissolved by both the reagents as compared with that dissolved by them at the temperature of 35°C. continuous. This is especially the case with the citrate solution, the dissolved phosphoric acid rising from 6.10 per cent. to 9.85 per cent., an increase of 3.75 per cent. This increase can be explained in two ways only: (1) Either the insoluble rock present is dissolved to this increased extent, or (2) there is a form of reverted phosphate present that is not fully taken up by either the citrate or oxalate solution at the lower temperature.

In order to ascertain if the former of these two explanations was the correct one, two separate portions of $\frac{3}{4}$ of a gram each of Navassa rock containing 0.120 gram P_2O_5, and corresponding to 6 per cent. of insoluble phosphoric acid when calculated on two grams as used in the above analysis (which is just the amount of apparently insoluble acid left in Series VII.), were rubbed to a paste in a mortar and treated each with 100 cc. of citrate of ammonia solution, the one at a temperature of 35°C. continuous for one hour, the other at a temperature falling from 70°C. to 40°C. during an hour, as in Series VIII. The following amounts of P_2O_5 were dissolved, calculated as per cent. on 2 grams:

SERIES IX.

No. 1.	Phos. acid dissolved,	1.16 per cent.
No. 2.	" " "	1.59 "

The increase in phosphoric acid dissolved by the use of the higher temperature is found to be only 0.43 per cent. It is seen at once that this small increase cannot explain the large increase of 3.75 per cent. in the case of the acid Navassa, made from the same rock.

The second of the two possible explanations, viz. the presence of a form of reverted phosphate not fully dissolved at 35°C., must therefore be the true one. The experiments already made show

that this form can be neither the dicalcic nor tricalcic phosphates, as the citrate solution is a perfect solvent for these two forms at a temperature of 35°C. The only form left is the reverted phosphate of iron and alumina. A quantity of the mixed normal phosphates of iron and alumina, Fe_2O_3, P_2O_5 and Al_2O_3, P_2O_5, was now prepared by precipitation. A portion was mixed with a large quantity of calcium sulphate and dried to a powder at a temperature not exceeding 60°C. The remainder was dried at the same temperature without admixture. One gram of the first portion containing 4 per cent. of phosphoric acid was now rubbed to a paste in a mortar and then digested with 100 cc. of the oxalate and citrate solutions, first at 35°C. and then at 70°C. to 40°C. for one hour.

SERIES X.

	P_2O_5 dis. at 35°C.	P_2O_5 dis. at 70° to 40°C.
Using oxalate of ammonia,	0.95 per cent.	3.20 per cent.
" citrate "	1.60 "	4.00 "

One gram of the unmixed portion containing on analysis 35.62 per cent. of phosphoric acid was now treated exactly in the same way, with results as follows:

SERIES XI.

	P_2O_5 dis. at 35°C.	P_2O_5 dis. at 70° to 40°C.
Using oxalate of ammonia	11.06 per cent.	26.50 per cent.
" citrate "	13.14 "	35.62 "

These two series of experiments prove the very important fact that neither the citrate nor oxalate solution will dissolve more than a small portion of the reverted phosphates of iron and alumina at the temperature of 35° C., and that even at the higher temperature of 70° C. to 40° C. the oxalate falls short of the perfect solvent power which must be required of it.

These results explain most clearly the great increase of phosphoric acid taken up in Series VIII. over that dissolved in Series VII. The acid Navassa under treatment contains a very large quantity of reverted phosphates of iron and alumina which are not dissolved at the lower temperature. They also explain why the citrate solution dissolves 1.30 per cent. more than the oxalate, because of its more vigorous solvent action on these forms of reverted phosphates. One gram of these phosphates of iron and alumina, treated with

100 cc. of the citrate solution at a continuous temperature of 65° C. for 30 minutes, formed also a clear solution.

In order to ascertain the amount of solvent action of this method upon the different forms of raw phosphates, ½ of a gram of each, corresponding to about 3 to 4 per cent. phosphoric acid when calculated upon two grams, was treated in the same manner as the above, temperature 70° C. to 40° C., using 100 cc. citrate solution.

SERIES XII.

	P_2O_5 dis.
Apatite	0.22 per cent.
South Carolina rock	0.61 "
Bone Ash	...
Navassa rock	1.09 "
Curaçao	2.07 "

Comparing this table with Series II., dividing the results there by ten, it is evident that at the higher temperature, only a small increase in the amount of insoluble rock dissolved is observed.

In this connection special attention is called to one point. Notice has been called to the fact that at 100° C. the oxalate solution loses ammonia and becomes decidedly acid in reaction. A solution of neutral oxalate, immersed in boiling water for one hour in an open beaker, acquired an acid strength of ½ per cent. oxalic acid; 100 cc. of the citrate of ammonia solution treated for an hour in the same way acquired an acid strength of 1.2 per cent. citric acid. The energy with which these acid solutions attack the undecomposed rock present in a superphosphate is shown in Series V. It is on account of these facts that Fresenius uses a neutral solution of the citrate salt and adopts the low temperature of 35° C., and Luck[1] in a second paper dwells with great emphasis upon this point in answer to the criticisms of a French chemist. But as the higher temperature is rendered indispensable on account of the presence of phosphates of iron and alumina in the great majority of superphosphates, this loss of ammonia and consequent acidity was prevented by digestion in a flask closed with a rubber cork.

The severest criticism upon the determination of reverted phosphates as an analytical process is the fact that when different quantities of substance are taken for analysis, different results are obtained. This most exceptional experience in chemical analysis,

[1] Zeitschrift für anal. Chem. **14.**

which is without a parallel in analytical determinations, requires a most careful examination, as this has done more than all else to cast discredit upon this analytical process. And yet it seems clear that this trouble can arise from only three sources:

(1) Either the fertilizer under treatment has so large an amount of reverted phosphate present that when a large amount is taken for analysis the citrate is unable to take it all up, but is able to do so when a smaller amount is employed, or—

(2) The citrate is an imperfect solvent for some form of reverted phosphate that may be present, either on account of the character of the latter, or on account of the method employed failing to dissolve it completely, the error showing more clearly as larger quantities are taken for the analysis, or—

(3) The discrepancy arises from the solvent action of the citrate upon the undecomposed rock present, a larger percentage of this being dissolved when smaller quantities are taken (*vide* Series I. and II.). The instances given by German experimenters, in the case of fertilizers containing 25 per cent. or more of phosphoric acid present as precipitated tricalcic phosphate, may be due mainly to the first of these causes. In such cases a smaller quantity must be taken, or it may be found that the higher temperature here recommended will so increase the solvent power of the citrate solution as to render this unnecessary. Whenever the phosphates of iron or alumina are present, it is evident from the experiments given that this discrepancy may be largely due to the second cause here assigned, namely, the method of the analysis, employing as it does the low temperature of 35° C. In order to ascertain whether the higher temperature of 70° C. to 40° C. will obviate the error from this second cause, 1, 2, 3, 4, and 5 grams of the above acid Navassa were treated each with 100 cc. of the citrate solution at this temperature, after the thorough washing out of the soluble phosphate.

SERIES XIII.

	P_2O_5 dissolved.	P_2O_5 undissolved.
Employing 1 gram substance	10.06 per cent.	1.94 per cent.
" 2 "	9.85 "	2.15 "
" 3 "	9.65 "	2.35 "
" 4 "	9.43 "	2.57 "
" 5 "	9.02 "	2.98 "

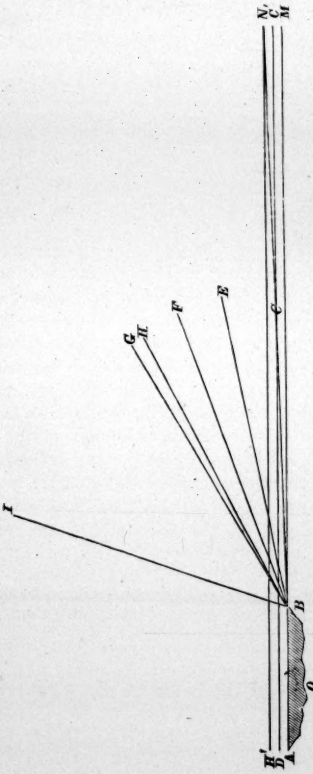
The very slight and uniform decrease of reverted phosphoric acid, about 0.20 per cent. for each additional gram taken, up to the 5 grams when the increase is a trifle larger, would certainly seem to show that every source of discrepancy but the third mentioned above had been obviated. When it is observed that in the last experiment 0.451 gram of reverted phosphoric acid is dissolved by the 100 cc. of citrate of ammonia solution at the temperature of 70° C. to 40° C., it certainly seems that nothing further could be desired as regards vigor of action upon the reverted forms. No other solvent suggested will approach the citrate solution in this important respect, when employed at the temperature here adopted.

But as regards the third cause of discrepancy it is very different. This cause lies in the very nature of things and cannot be overcome. No reagent can be found that will dissolve the strictly reverted phosphates and not affect the undecomposed rock present. Nor is it desirable that any such reagent should be found, nor would it be just to employ it in case it were possible to find it. The whole idea upon which the determination of reverted phosphates rests is that the solvent action of the liquids of the soil is stronger than that of pure water, and is closely imitated by the solvent action of the organic salts of ammonia. Now there is a certain percentage of the raw phosphates that will always be taken up by this increased solvent power, and this percentage is practically and with justice considered equal in value to and reported as reverted phosphate.

The only difficulty that now presents itself is to so fix the amount of substance taken for analysis that the solvent action of the citrate solution upon the undecomposed rock shall dissolve such a percentage of this as shall when reported as reverted phosphate be a fair equivalent of its agricultural value. This conception here stated will be best illustrated by the accompanying diagram. 2 grams of the five forms of raw phosphates were treated with 100 cc. of citrate of ammonia solution at a falling temperature 70° C. to 40° C. for one hour, also two grams of the reverted phosphates of iron and alumina containing 35.62 per cent. of phosphoric acid. The latter was dissolved to a clear solution.

SERIES XIV.

Apatite,	Phosphoric acid dissolved,		0.60	per cent.
South Carolina rock,	"	"	2.62	"
Bone Ash,	"	"	3.15	"
Navassa,	"	"	3.75	"
Curaçao,	"	"	7.50	"
Reverted phos. of iron and alumina,	"	"	35.62	"



In the diagram use is again made of the figure of speech previously employed. AOB is the river bed, representing the phosphates soluble in water, completely covered by the line AM, the height of which represents the solvent power of water. The line BC represents the flats or the reverted phosphates lying just above the water, and slightly rising, since the different forms possess different degrees of solubility. The line DC′ represents the solvent power of 100 cc. of citrate of ammonia solution at the temperature 70° C. to 40° C. The lines BE, BF, BH, BG and BI represent the banks rising at different angles, or the different raw phosphates, Curaçao, Navassa, Bone Ash, South Carolina rock, and Apatite here examined. These lines are all two inches in length, to represen the two grams of substance taken. All of BC falls below DC or becomes soluble in the citrate solution, $\frac{1}{4}$ of BE, $\frac{1}{8}$ of BF, $\frac{1}{20}$ of BH, $\frac{1}{10}$ of BG, and $\frac{1}{30}$ of BI, calculating from 30,

30, 36, 27, and 42 percentages of phosphoric acid present in the five samples.

Now suppose one gram of the above substances be taken to 100 cc. of citrate solution. This proportion is the same as 200 cc. citrate solution to the 2 grams of substance taken in the diagram. The line DC will be raised to H'N, twice as far above the surface of the water. Twice as large an amount of reverted phosphates will be taken up, viz. BN, and at the same time nearly twice as large an amount of the raw phosphates as shown in the figure. Thus repeating Series XIV., using however one gram of substance, there were dissolved as follows:

SERIES XV.

Apatite,	Phosphoric acid dissolved,	1.06	per cent.
South Carolina rock,	"	"	...
Bone Ash,	"	"	5.20 "
Navassa,	"	"	6.20 "
Curaçao,	"	"	11.50 "

Attention is called to the nature of Curaçao phosphate as brought out in this connection. Since by successive treatments with citrate of ammonia solution, or by employing a very small quantity for analysis, as $\frac{1}{10}$ of a gram, nearly all of this can be brought into solution, many chemists regard its phosphoric acid as nearly all in the available form, and an analysis made by one chemist on the identical sample used in this work reports the presence of 18 per cent. of reverted phosphoric acid. But the whole course of experiments given in this paper shows conclusively that it differs from the other raw phosphates only in degree of solubility, and is very far removed as regards this property from the true reverted forms, being, as shown in the diagram, based upon Series XIV., only $\frac{1}{3}$ as soluble at the best as the latter, and only about twice as soluble as Navassa rock and bone ash.

It seems almost certain from the agricultural experiments described in the last edition of Johnston's "Agricultural Chemistry," on the use of finely ground raw phosphates, that all the phosphoric acid in such phosphates becomes ultimately soluble in the soil. The division of phosphates therefore into the three forms, soluble, reverted, and insoluble, will have reference only to the time required to render them available for plant use. Supposing, in the

above diagram, that the solvent action of 100 cc. of the citrate solution represents the solvent action of the liquids of the soil for a certain period of time, as *e. g.* one season, upon the forms of phosphate there represented, it is evident that all the soluble and reverted would be available the first season, that raw Curaçao would all be rendered available in something over five seasons, the Navassa in eight seasons, and so on. The divisions, therefore, of soluble, reverted, and insoluble become indispensable as means of fixing commercial and agriculturnl values.

In conclusion, emphasis is laid upon the following points as brought out in this inquiry:

I. While the line of division between the reverted forms and the original insoluble forms of phosphoric acid may be sharply drawn in the case of an extremely insoluble phosphate, like apatite, in the case of the more easily soluble natural phosphates the two great classes overlap, one the other. Whatever solvent therefore is used for determining reverted phosphates, the same will also dissolve a small percentage of the undecomposed phosphate that may be present; this percentage varying considerably according to the character of the insoluble phosphate. This percentage, representing as it does the comparative solubility which such insoluble phosphate possesses to the true reverted phosphates present, is justly considered as equivalent to an equal amount of the true reverted forms, and reported as such.

II. A slightly ammoniacal citrate of ammonia solution, alone of all the solvents that have been proposed, is a perfect solvent for all the forms of reverted phosphate, while at the same time not unduly dissolving the raw or insoluble phosphates present. Such a solution dissolves but a trace of the most difficultly soluble form of phosphate known, viz. apatite, and dissolves the other natural phosphates to a greater and greater extent as they approach in character the true reverted forms.

III. Neither the "Washington method" (method of Fresenius) nor the "Cincinnati method" can be relied upon to take up all the reverted phosphates that may be present.

IV. A modification of the method of Fresenius, consisting of the use of a higher temperature for the digestion, will meet all the requirements of the case, provided that the greatest care is taken to guard against acidity of the solvent and consequent excessive solution of the insoluble phosphates present. Whether the falling

temperature of 70° C. to 40° C. as here explained, or a continuous temperature of 65° C. for 30 minutes, be used, there will be but slight if any differences in the results, provided that the solution of citrate be slightly ammoniacal, and the digestion be made in a closed flask. To the use of *acid* solutions of citrate, either acid at the beginning of the digestion or becoming acid during its continuance, are probably due, more than to any other cause, the discrepancies in this analytical process.

Laboratory of Stillwell and Gladding, New York.

COLUMBITE, ORTHITE AND MONAZITE FROM AMELIA CO., VIRGINIA.

By F. P. Dunnington.

Among the minerals found with microlite (see Vol. 3, No. 2, of this Journal) one variety of columbite attracted attention by its decided red color when in thin splinters. It proved to have the following properties: Hardness, 5.5; specific gravity, 6.48; lustre, sub-resinous; color, dark brown; streak, light brown.

Analysis gave the following results:

Ta_2O_5, Nb_2O_5, SnO_2—trace	84.81
MnO,	8.05
FeO,	5.07
CaO,	1.27
MgO,	.20
Y_2O_3(?)	.82
	100.22

The excess of the manganese over the iron is peculiar, and probably accounts for the unusual red color of the splinters and light color of streak.

The specific gravity of the mixed acids = 6.51. Pure Ta_2O_5 and Nb_2O_5 similarly ignited respectively gave the specific gravities 7.87 and 4.20, from which data we obtain an approximate estimation of the amounts of the acids:

Ta_2O_5, 53.4, and Nb_2O_5, 31.4 per cent.

The oxygen ratio for the metallic acids and the bases will then be:

$$Ta : Nb : R = 27 : 26 : 10,$$

thus affording a formula in which the molecular ratio of Nb_2O_5 to $Ta_2O_5 = 1 : 1$.

In Dana's Mineralogy there have been observed the ratios:

$$Nb_2O_5 : Ta_2O_5 = 2 : 1,\ 3 : 1 \text{ and } 4 : 1.$$

As may have been expected from the above analysis, the specific gravity of this mineral is greater than that of any of the specimens whose analyses are quoted by Prof. Dana.

Orthite also is found in this locality. It occurs in blade-like crystals several inches in length; the faces of the crystals being partly decomposed, no accurate measurements of the angles could be made. Hardness, 5.5; specific gravity, 3.323; lustre, pitchy; color, greyish black; streak, greenish grey. It fuses with much intumescence, and is gelatinized by hydrochloric acid without applying heat. Analysis gave the following:

SiO_2,	32.35
Al_2O_3,	16.42
Fe_2O_3,	4.49
Ce_2O_3,	11.14
La_2O_3,	3.47
Di_2O_3,	6.91
FeO,	10.48
MnO,	1.12
CaO,	11.47
K_2O, Na_2O,	.46
H_2O,	2.31
	100.62

Monazite also is found in this locality. It was first identified by Dr. G. F. Koenig, who published a notice of it in the Proceedings of the Academy of Natural Sciences of Philadelphia, Jan. 24, 1882.

Before seeing this notice, I made an analysis of a specimen of the mineral in question, and as this shows the presence of thorina, not before noticed, I give my results:

Ce_2O_3	16.30
Di_2O_3	24.4
La_2O_3	10.3
Y_2O_3	1.1
Fe_2O_3	.9
Al_2O_3	.04
[1]ThO_2	18.6
P_2O_5	24.04
SiO_2	2.7
	98.38

If we exclude the thorina and silica, we shall have for the remaining constituents, approximately, the formula $R_2'''P_2O_8$; hence it is possible that the thorina may occur in the form of orangite, but the analysis has not been made with sufficient accuracy to decide this point.

UNIVERSITY OF VIRGINIA, *March*, 1882.

Laboratory Notes from the University of Cincinnati.

XXVI.—A NEW MINERAL FROM COLORADO.

BY F. W. CLARKE AND N. W. PERRY.

A few months ago one of us received from an assayer at Gunnison city a peculiar mineral which had been brought in for examination from a point about twenty miles to the southward of that place. It was said to exist in considerable quantity, and information was sought as to its probable value; but no details as to its mode of occurrence or associations were given.

[1] Sp. grav. = 7.5; hence not pure.

The mineral is massive, easily scratched by the knife, and deep purple in color. In powder the purple tint is retained. At first sight it suggests yttrocerite, a fact which led us to immediately examine it for fluorine. It is associated with a semi-massive calcite, which in portions is tinged with ferric oxide. Although the mineral forms a distinct layer upon the calcite more than a centimetre in thickness, it is so penetrated by the latter species that we could not effect a complete mechanical separation of the two substances. Hence a correction for admixed calcite has to be applied to the results of actual analysis. Sp. gr. 2.85.

The analysis was made under our direction, by Mr. E. A. Kebler, with the following results:

Fluorine,	31.96
Calcium,	45.91
Silica,	6.02
Alumina, (+ tr. Fe_2O_3),	5.21
Carbon dioxide,	5.61
Soda,	.74
	93.45

The loss is oxygen, which should be reckoned as united with a part of the calcium. A second fluorine estimation gave 31.86 per cent. Assuming that the fluorine and carbonic acid are wholly united with calcium, and recalculating the remainder of the calcium as oxide, the foregoing results may be stated as follows:

CaF_2,	65.60
$CaCO_3$,	12.75
CaO,	10.02
SiO_2,	6.02
Al_2O_3,	5.21
Na_2O,	.74
	100.34

If we regard the calcium carbonate as being merely admixed calcite, and recalculate the balance of the analysis, we have for the mineral the following composition:

CaF_2,	74.89
CaO,	11.44
SiO_2,	6.87
Al_2O_3	5.95
Na_2O,	.85
	100.00

These figures agree very closely with the following formula:

$$7CaO.2Al_2O_3.4SiO_2.32CaF_2.$$

Possibly an analysis of purer material might give the simpler ratio:

$$4CaO.Al_2O_3.2SiO_2.16CaF_2.$$

Whether or no the mineral is a definite and distinct species can be determined only by additional investigation. The locality at which it was found ought to be carefully studied, and the associated minerals examined. Probably the mineral is an alteration product of fluor spar, although it may be only a mixture of that species with a silicate. Still, with the exception of the admixed calcite, the mineral seems to be homogeneous, and the color of its powder is unlike that of fluorite. If it should finally be established as a new species we shall propose for it the name of gunnisonite.

ON THE OXIDATION OF SUBSTITUTION PRODUCTS OF AROMATIC HYDROCARBONS.

By Ira Remsen.

XI.—OXIDATION OF METATOLUENESULPHAMIDE.

By Chase Palmer.

It has been shown in earlier papers of this series that oxidizable groups situated in the meta-position relatively to negative groups in benzene are converted into carboxyl, apparently with the same readiness as similar groups in the para-position. In the cases described, however, the influence of the negative groups has been, to some extent, concealed by the presence of ortho-groups. As it

is established with a fair degree of certainty that acid oxidizing agents tend to transform para-groups and leave ortho-groups unchanged, and that alkaline oxidizing agents tend to transform ortho-groups and leave para-groups unchanged, it remains to be determined whether meta-groups more closely resemble those in the ortho- or those in the para-position with respect to their conduct under the influence of oxidizing agents.

For the purpose of this study the amide of metatoluenesulphonic acid was selected. The acid was prepared according to the directions given by Hübner and Müller,[1] by introducing a sulpho-group into orthobromtoluene, and then substituting hydrogen for bromine in the product. One part of orthobromtoluene (obtained from Kahlbaum and still containing some of the para-compound) was added gradually to three parts of fuming sulphuric acid. The calcium salt of the sulphonic acid was converted into the sodium salt. The solution of the latter was kept in contact with weak sodium amalgam for ten days, fresh amalgam being added as soon as the evolution of hydrogen stopped. The organic salt in solution was then found to be free from bromine. The solution was neutralized with sulphuric acid and concentrated, when a large quantity of sodium sulphate crystallized out. After as much as possible of the inorganic salts had been removed, the last mother liquor was evaporated to dryness. The dried residue was treated with phosphorus pentachloride, and the chloride thus formed boiled with concentrated aqueous ammonia. The sulphamide was extracted with ether and purified by repeated recrystallizations from water. The product contained a not inconsiderable quantity of ortho-toluenesulphamide, the presence of which is readily accounted for by the fact that the bromtoluene used in the experiment contained some of the para-compound. When sulphuric acid acts upon para-bromtoluene, the product formed contains the sulpho-group in the ortho-position relatively to the methyl, so that when the bromine is removed the product must be ortho-toluenesulphamide. The meta-amide, after purification, had the properties ascribed to it by Hübner and Müller,[2] its fusing point being 90°–91°.

Conduct towards Potassium Permanganate.

To determine the influence of an oxidizing agent in alkaline solutions, a mixture was made consisting of five grams of pure meta-

[1] Zeitschrift für Chemie, 1870, 449; 1871, 14; and Annalen der Chemie, **169**, 47.
[2] *Loc. cit.*

toluenesulphamide and twenty grams potassium permanganate dissolved in five hundred cubic centimeters of water. The solution was made slightly alkaline. The whole was heated on a water bath for about twenty hours before the action ceased. When no further action seemed to take place, the slight excess of permanganate was reduced by means of a few drops of an aqueous solution of sulphur dioxide. The precipitated manganese hydroxides were filtered off, and the filtrate acidified with hydrochloric acid. On cooling an acid crystallized out in scales. The substance was purified by two or three crystallizations from hot water. It fused at 235° (uncorrected), at the same time suffering partial decomposition. It was converted into the barium salt by boiling the solution with barium carbonate. The salt crystallized from the concentrated solution. Dried over sulphuric acid its analysis gave results as follows:

0.4728 gram salt lost 0.0557 gram H_2O at 120°, and gave 0.1776 gram $BaSO_4$=0.1044 gram Ba.

	Calculated for $\left(C_6H_4\begin{cases}SO_2NH_2\\CO_2\end{cases}\right)_2Ba+4H_2O$.			Found.
$(C_7H_6SO_4N)_2$	400	65.69	...	...
Ba	137	22.49	...	22.08
$4H_2O$	72	11.82	...	11.78

The acid thus formed is identical with that described under the name of sulphobenzamic acid by Limpricht and Uslar,[1] and later by Engelhardt.[2] The former obtained it by heating sulphobenzamide, $C_6H_4\begin{cases}SO_2NH_2\\CONH_2,\end{cases}$ or ammonium ethylsulphobenzoate with potassium hydroxide; and by treating the compound $C_7N_2H_6SO_2$ (obtained from sulphobenzamide by treatment with phosphorus pentachloride) with potassium hydroxide. Engelhardt obtained the acid by treating benzonitrile with sulphur trioxide. The identity of our product with "sulphobenzamic" acid was proved by comparing it directly with the acid prepared according to the method of Limpricht and Uslar. No difference was observed between them. The method of formation above described shows clearly that the substance is *metasulphaminebenzoic acid*, $C_6H_4\begin{cases}SO_2NH_2\\CO_2H.\end{cases}$ The name sulphobenzamic acid is incorrect, as it applies only to a substance in which the amide group is in the carboxyl, viz. $C_6H_4\begin{cases}SO_2OH\\CONH_2.\end{cases}$

[1] Annalen der Chemie, **106**, 27. [2] Journal für praktische Chemie, **75**, 363.

The principal feature of interest to be noted in the oxidation experiment is the fact that the action does not take place readily. The oxidation of ortho-toluenesulphamide with permanganate takes place very easily, that of the para-amide with difficulty. As nearly as could be judged the oxidation of a given quantity of the meta-amide required about the same time as the same quantity of the para-amide under the same conditions of temperature and dilution, and a much longer time than the ortho-amide.

Conduct towards Chromic Acid.

The mixture used consisted of five grams of pure meta-toluenesulphamide, fifteen grams of potassium pyrochromate, and twenty grams of concentrated sulphuric acid diluted with three times its volume of water. The flask containing the mixture was heated on a water-bath for about an hour, when the action was found to be complete. A crystallized product appeared in the mixture. After diluting with water and cooling, the acid formed was filtered off and purified by crystallization from water. As was expected, the product was identical with the meta-sulphamine-benzoic acid described above. The barium salt was made and analyzed.

0.339 gram of the salt lost 0.0383 gram H_2O at 120°, and gave 0.1263 gram $BaSO_4$.

	Calculated for $\left(C_6^*H_4\begin{cases}SO_2NH_2\\CO_2\end{cases}\right)_2Ba+4H_2O$.		Found.
$(C_7H_6SO_4N)_2$	400	65.69	...
Ba	137	22.49	22.24
$4H_2O$	72	11.82	11.47

From this experiment the conclusion may be drawn that the meta-amide conducts itself towards chromic acid in very much the same way as the para-amide.

In general, then, the conduct of meta-toluenesulphamide towards both alkaline and acid oxidizing agents is like that of the para amide, and no resemblance is noticed between its conduct and that of the ortho-amide. Whether the same is true of all meta compounds it is impossible to say, but judging from the fact that all para-compounds conduct themselves in the same way towards oxidizing agents, and that what is true of one ortho-compound is true of others, the conclusion is probable that with reference to their conduct under the influence of oxidizing agents, meta-compounds are allied to para- and not to ortho-compounds.

REVIEWS AND REPORTS.

Recent Progress in Agricultural Science.

[Continued from Vol. **3**, 145.]

Assimilation.—In its strict sense, assimilation in plants means the process of forming new organic matter out of inorganic materials by the aid of the sun's rays, and is peculiar to chlorophyl-bearing plants. It will be convenient, however, to give the term a somewhat more extended meaning, and to apply it not only to this process, but also to those related processes which furnish the materials for true assimilation, and to consider in the same connection the kinds and sources of these materials.

Essential Elements.—The question what elements are necessary for the growth of the higher plants may be considered as practically settled. A few points may, however, be noted in passing. As is well known, the earlier experiments showed potassium to be one of the elements essential to plant growth, and it was natural that the question should arise whether the functions of this element in the plant could not be performed by other of the alkali metals. Experiments with sodium showed that this element was incapable of taking the place of potassium, and Nobbe has shown that lithium acts as a direct poison to plants. The physiological worth of these three elements increases with their atomic weight: may it not be possible that other elements of the same group having a higher atomic weight may have a still higher worth? An answer to this question has been attempted by Loew,[1] in some water-culture experiments on buckwheat with rubidium. Earlier experiments by Birner and Lucanus with rubidium, gave very unfavorable results, but according to Loew, the abnormal appearances in their plants were exactly those observed by Nobbe to result from the absence of chlorine; and as only rubidium nitrate was used, it was thought desirable to make similar experiments with the chloride, as well as to repeat those with the nitrate.

The latter gave an entirely negative result; but the experiments with the chloride, in comparison with potassium chloride, though not fully successful, seem to show that at least a certain amount of growth may be made by the aid of rubidium. Still better results were obtained in a third experiment in which a much smaller amount of rubidium was used, in the form of nitrate, with the addition of ammonium chloride. In both experiments the plants

[1] Landw. Versuchs-Stationen, **21**, 389.

grew well until the time of fruiting, and from then on fell behind the potassium plant. The plant nourished with rubidium chloride formed no seeds, and that fed with the nitrate only one; but whether this was due to abnormal nutrition or to some other cause does not clearly appear. On the whole the results, though not conclusive, seem to indicate the *possibility* that suitable quantities of rubidium in a properly constituted solution may be able to take the place of potassium.

Another old question which has lately received renewed attention, is that of the necessity or utility of silica to the plant. As regards its necessity, the newer experiments have only confirmed the results of the older ones that silica is entirely non-essential. A somewhat striking proof of this has been given by Höhnel.[1] The pericarp of *Lithospermum arvense* is normally very rich in silica, containing from 13 to 16 per cent. of this substance, while its outermost layers contain probably 70 per cent. Höhnel has, however, succeeded in producing, by means of water culture, ripe seeds of this plant containing at most but minute traces of silica.

It appears, however, from recent experiments that silica, though not essential to the plant, is nevertheless serviceable to it. In Höhnel's experiments it was noticed that the plants grown without silica suffered from plant lice, while neighboring plants which received silica were not thus affected.

Some experiments by Wolff show that silica has more important functions than the simple protection of the plant. Experiments on the growth of the oat plant in aqueous solutions,[2] continued through fourteen years, have led him to the conclusion that silica favors the seasonable and uniform ripening of the grain by causing the death of the leaves at the proper time, which is followed by a translocation of the nutritive matters contained in them to the seeds. Thus in an experiment without silica 30 seeds were produced, with a little silica 90, and with much silica 184. Another function of silica was also revealed in some of these same experiments. The experiments were directed towards ascertaining the minimum amount of the several ash ingredients necessary for the production of an average crop.[3] Thus it was found that the amount of potash could be reduced to about 0.8 per cent. of the dry weight of the plant, that of phosphoric acid to about 0.5 per cent., &c., &c. It was found impossible, however, to produce a single plant which contained *all* the ash ingredients in the minimum quantity. The total ash, it was found, must always be considerably in excess of the sum of the minima of each ingredient. Only when some indifferent mineral substance, like silica, was supplied to the plants, could a normal growth be obtained with the minimum amounts of the other ingredients. The *rôle* of silica in this respect can also be assumed by lime or by phosphoric acid; but these substances,

[1] Haberlandt's Wiss. prakt. Untersuchungen, **2**, 160.
[2] Jahresber. Agr. Chem. N. F. **3**, 216.
[3] *Ibid.* 18–19, **1**, 250.

especially the latter, are somewhat costly, while silica is present in an assimilable form in all soils in greater or less quantity. It would thus appear that while silica is not essential to the *plant*, it may be of great importance to the *crop* by enabling it to make a satisfactory growth in a soil which, without the silica, would not furnish a sufficient supply of ash ingredients, or by preventing a useless consumption of phosphoric acid or other ash ingredients, and an unnecessary exhaustion of the land.

Sources of Plant Food.—That the *carbon* of vegetation is chiefly supplied by the carbon dioxide of the atmosphere has become one of the truisms of botany; but the question whether this is the sole source of the carbon of agricultural plants and crops, or whether the numerous carbon compounds existing in most fertile soils contribute to any considerable extent to their nourishment, is one that has given rise to no little discussion. The well-known experiments of De Saussure and others (compare Johnson's "How Crops Feed," pp. 232 *et seq.*) render it extremely probable that the organic matters ("humus") of the soil may be assimilated by plants, as we know that certain nitrogenous organic matters may be.

Some later experiments point in the same direction. Van Tieghem[1] finds that the embryo of *Mirabilis jalappa* will grow when the endosperm is removed and replaced by a paste of albumin and water, or of potato starch and water, containing the necessary inorganic nutrients. By microscopical examination and otherwise, Van Tieghem satisfied himself that these substances were actually assimilated. From the brief account of these experiments accessible to the writer it is impossible to judge of their accuracy or of the weight which is to be given them, and Böhm[2] on repeating them obtained negative results; but Blociszewski[3] has since repeated and extended them with much the same result as Van Tieghem. Embryos of rye and peas, separated from the endosperm or cotyledons, assimilated starch and sugar, and grew, not indeed as well as those of whole seeds, but decidedly better than those which received no artificial food. The starch grains which lay next to the scutellum of the rye or the epidermis of the radicle of the pea were found to have been attacked and almost entirely dissolved. Embryos of rye also grew when nourished with their own finely-ground endosperm, while embryos of the pea grow no better when embedded in pellets of their own ground cotyledons than without this addition. The pea embryos, on the other hand, seemed to be aided in their growth by a dilute solution of asparagin, while this substance appeared to be of no use, or even harmful, to the rye embryos.

It thus appears that plants may assimilate "organic" matter not only when full grown but also in the first stages of their existence.

[1] Jahresber. Agr. Chem. 16–17, **1**, 259.
[2] Landw. Jahrbücher, **5**, 145.
[3] Jahresber. Agr. Chem. 18–19, **1**, 247.

A few trials have been made by Stutzer[1] to ascertain what classes of organic substances may be assimilated. He experimented chiefly on young plants of *Brassica rapa*, growing them in an artificial soil composed of sand or pumice-stone and calcium oxalate or tartarate, moistened with a solution of the needful inorganic ingredients. The plants were placed under bell-glasses, from which the carbon dioxide of the air was excluded. They grew vigorously and gained as much as 228 per cent. of dry matter, thus showing that these acids served in some way as a source of carbon. It was possible, however, that they were first oxidized in the plant to CO_2 which was then assimilated, and to test this a second series of experiments was made in the same way, except that a dish of concentrated solution of sodium hydrate was placed inside each bell-glass. Under these circumstances the plants cultivated in the calcium oxalate speedily died and showed a loss of 4 to 7 per cent. of their dry weight in ten or twelve days, thus showing that the oxalic acid could not be utilized as such by the plant, but must first be oxidized to CO_2. The calcium oxalate remaining after these experiments contained notable quantities of carbonates. The plants cultivated in the calcium tartarate, however, behaved differently. Here a growth took place, and an increase in the dry weight of 66 and 69 per cent. in 17 days was obtained.

Other plants, cultivated in the same soil but with only the atmospheric CO_2 excluded, gained fully twice as much in the same time. In all cases the roots were found encrusted with calcium carbonate. This formation of calcium carbonate, Stutzer suggests, may be explained as due to a metathetical reaction between the soluble carbonates of the roots and the oxalate or tartarate of the soil. The different behavior of oxalic and tartaric acid in these experiments Stutzer explains by a reference to their chemical constitution. Oxalic acid consists of two carboxyl groups, from which, apparently, the plant is unable to appropriate carbon directly. Tartaric acid, on the other hand, contains two carboxyl and two alcoholic groups, and from the latter, according to Stutzer, the plant can assimilate carbon without the necessity of a previous oxidation to CO_2. When the plants were cultivated in a bell-jar containing sodium hydrate, only half the carbon of the tartaric acid could be utilized, and a large amount of CO_2 was found in the sodium hydrate solution at the close of the experiment. In the case in which the sodium hydrate was omitted, however, the carbon of the carboxyl groups was also available, being first oxidized to CO_2 and exhaled, and then assimilated by the chlorophyl grains. Hence, the growth in the latter case was about twice as great as in the former, corresponding roughly to the greater amount of assimilable carbon at the disposal of the plant. A confirmation of this hypothesis was given by an experiment in which

[1] Landw. Versuchs-Stationen, **21**, 93.

glycerine was the sole source of carbon. A gain of 126 per cent. of dry substance was made in seventeen days.

As numerous difficulties had to be overcome in experiments of this sort on higher plants, the investigation was continued with chlorophyl-free plants, chiefly with *Penicillium glaucum*, in which, if growth took place at all, it must be at the expense of the "organic" carbon. It was found that oxalic and formic acids, that is, acids containing only carboxyl groups, were incapable of nourishing this plant. Acetic acid and acetates produced an abundant growth, as did also succinic acid. Succinate of iron was also found capable of furnishing carbon to plants of *Brassica rapa* in an atmosphere free from CO_2. Ethyl alcohol, glycerin, sugar, malic acid, citric acid, lactic acid and tartaric acid caused an abundant growth of the fungus, as, according to Stutzer's hypothesis, they should do; but butyric acid, valerianic acid, and amyl alcohol formed noteworthy exceptions, neither sustaining *penicillium* themselves nor permitting its growth in solutions to which glycerin or sugar had been added.

Stutzer's experiments have been repeated by Schmöger,[1] who obtained similar results, but does not regard them as conclusive, since, according to his experiments, the method adopted includes a grave source of error. This source of error lies in the fact that both oxalate and tartarate of calcium are very easily decomposed by the action of bacteria or other organisms into calcium carbonate and carbon dioxide, so that the soil in Stutzer's experiments was a continual source of CO_2. Schmöger found that moist mixtures of calcium oxalate or tartarate with solution of plant food and with sand (the latter may be omitted) contained, after being exposed to the air for some twenty days, very considerable quantities of calcium carbonate and an abundance of bacteria resembling *Bacterium termo*. Similar mixtures were placed in two flasks, heated to boiling on the water-bath, and stoppered with cotton heated to 120°. Two other flasks were filled in the same way, but not heated. One of each pair was opened after twenty days. The contents of the boiled flask contained no CO_2, those of the unboiled flask 0.234 gram. After thirty-four days the other boiled flask contained no CO_2, and the other unboiled one 0.2675 gram. Schmöger also determined the amount of CO_2 absorbed by the potash solution in his vegetation experiments, as well as the combined CO_2 remaining in the soil, and found the two to be approximately equal. In experiments with plants grown in sand alone, the amount of CO_2 exhaled was found to be very small. Schmöger, therefore, concludes that the growth obtained by Stutzer and himself in those experiments in which no potash was present was made by means of the CO_2 exhaled by the artificial soil, and that it is very possible that the small growth obtained in the presence of potash was due to small portions of CO_2 which escaped absorption.

[1] Jour. f. Landw. **28**, 179.

At any rate, in the absence of proof that the experiments were really made in an atmosphere free from CO_2, they furnish no evidence of a direct assimilation of organic carbon compounds by the higher plants.

Experiments with such organic matters as are found in the soil have in general given negative results. Detmer[1] claims to have observed microscopically an absorption of some of the oxidation products of humus (crenic or apocrenic acids) by the rootlets of young peas, and thinks it probable that they contributed to the nourishment of the plants.

Böhm[2] has sought to solve the question by investigating whether bean plants, freed from starch by long vegetation in the dark, could produce starch when supplied with carbon only through their roots. Negative results were obtained in all cases. No starch formation could be detected, and plants grown in a garden soil containing humus lived no longer than those grown in pure sand (with addition of inorganic nutrients).

Moll[3] has made similar experiments and obtained the same result. In no case was the least formation of starch observed, but on the contrary, starch disappeared from leaves containing it when they were placed in an atmosphere free from CO_2, although they remained in connection with the plant, which grew in a moist soil, rich in humus, and presumably containing much CO_2. Leaves were also separated from the plants and arranged with the basal end in an atmosphere containing about 5 per cent. of CO_2, while the upper end was in an atmosphere kept free from this gas. In some cases an intermediate portion of the leaf was exposed to the air, and in others not. The leaves having been made starch-free in the first place, not the least formation of starch could be detected in the portion of the leaf deprived of CO_2, although it took place vigorously in the other portion of the leaf. Comparative experiments were also made on the rapidity of starch formation in starch-free leaves. A leaf was divided lengthwise just at one side of the midrib. One portion was freely exposed to the air, while the base of the portion containing the midrib was surrounded with an atmosphere containing 5.5 per cent. of CO_2. It was found that this abundant supply of CO_2 to the lower end of the leaf was unable to accelerate at all the starch formation, but that the latter went on at sensibly the same rate as in the other half of the leaf. It was likewise found that the CO_2 of the soil was equally unable to accelerate the formation of starch in the leaves. It would, therefore, appear that CO_2 cannot be transferred as such in the plant, even through very short distances, and also that the organic matter in the soils used by Moll was not able to contribute appreciably to the nourishment of the plants. Corenwinder,[4] however, has observed that the leaves of a branch of a young chestnut tree, which

[1] Jahresber. Agr. Chem. 13–15, **2**, 166.
[2] *Ibid.* 18–19, **1**, 247.
[3] Landw. Jahrbücher, **6**, 327.
[4] Jahresber. Agr. Chem. 18–19, **1**, 299.

was enclosed in an atmosphere free from carbonic acid but not severed from the tree, developed normally, from which fact he concludes that they were nourished by carbonic acid dissolved in the sap. Moll's results certainly throw serious doubt on this conclusion, and it is quite as reasonable to suppose that a transfer of plastic materials from the remainder of the tree took place.

The experiments of Böhm and Moll, as well as the very similar ones of Cailletet,[1] while they do not conclusively show that plants may not assimilate carbon from organic compounds, do show that under ordinary circumstances and in ordinary soils the amount of carbon which plants obtain through their roots is at least too small to be of any practical significance. The undoubted value of the humus of the soil and of manures lies partly in the inorganic matters which it contains, but to a far larger degree in the solvent action of the carbonic acid generated by its decay, and in its influence on the physical properties of the soil.

H. P. ARMSBY.

(To be continued.)

A TREATISE ON CHEMISTRY. Vol. III. THE CHEMISTRY OF THE HYDROCARBONS AND THEIR DERIVATIVES; or, ORGANIC CHEMISTRY. Part I. By H. E. ROSCOE and C. SCHORLEMMER. New York: D. Appleton & Co. $5.00.

The volume of Roscoe and Schorlemmer forms the first part of the third volume of the excellent "Treatise on Chemistry," and in it the consideration of organic chemistry is begun. The authors give a new name to the subject. That in common use is "The Chemistry of Carbon Compounds," but this they claim, and justly, is too broad, as it applies to all the simple compounds of carbon, such as carbonic acid and the whole list of carbonates, which enter so largely into the composition of the inorganic portions of the earth. They adopt the name "Chemistry of the Hydrocarbons and their Derivatives," and it is hard to see what rational objection can be made to this. It certainly describes accurately what it is intended to describe, and this is more than can be said of any of the names now in use. It may be firmly stated that this book is the most readable one on the subject that has appeared in any language; and this is a very great merit. Hardly a single one of its many predecessors can be *read*. One may serve admirably as a book of reference for the investigator, another as a laboratory guide, and a third as an aid in connection with lectures; but they cannot be read continuously with much advantage to the reader. The authors have dealt with their subject in a broad way. They have, of course, first had in mind the pure science, and they have

[1] Jahresber. Agr. Chem. 13-15, **2**, 166.

endeavored to point out the methods of the science, as well as to give the results of the application of these methods. Admirable descriptions of the facts of the subject are given, with sufficient fulness for the purposes of most students; and references to the sources of information, the original articles in the chemical journals, are found in connection with every important point. Further, the industrial applications of the science receive full attention, not in an off-hand way as is usual, but in such a way as to bring out their full importance. The chapters on petroleum, alcohol, ether, vinegar and soap should be specially mentioned in this connection. The subject of alcohol regarded in its industrial aspects occupies about forty pages of very interesting reading matter. Then, too, the historical side of the science is treated with great clearness and in an interesting way. There is first an introductory chapter which treats of the development of the subject as a whole, and then, as each new group is brought forward, the special history of this group is given. Thus far only one main group of compounds has been considered, viz. the paraffins, or the marsh gas series of hydrocarbons and their derivatives. If the other groups are treated as fully as this one, and considering their importance it is probable that they will be, the completed treatise will be by far the most extensive one in the English language. As regards the way in which the theories are presented, it is plain that the authors have tried to be consistent, and they have succeeded in this better than most other writers; but exception may be taken to some points. It is quite impossible here to discuss the matter in detail, and a few examples must suffice for illustration. The "law of the linking of atoms" is fundamental, and was, of course, discovered through a study of facts established in connection with a very large number of carbon compounds. A proper study of these facts will show clearly that the law is a just induction. The connection between the facts and the law is, however, not made clear by the paragraph on pages 112 and 113. The following sentence occurs on page 129: "This is caused by the rupture of one of the links of a double-linked carbon atom." The language is highly figurative, and though there are certain phenomena known which correspond to this language in some way, the character of these phenomena is too little understood to warrant the use of such expressions as "rupture of links." Surgical chemistry is a subject for which we are not quite prepared. The language is not original with the authors; it is the every-day language of chemistry, and when used cautiously is not dangerous; but it is not right to introduce it in the early part of a text-book, before the exact nature of the facts to which it refers has been explained. But the book is not one to put the reader in a fault-finding mood. The character of Part I. is such that we await with feelings of pleasurable expectancy the appearance of the concluding parts of the volume.

I. R.

ADOLPH STRECKER'S SHORT TEXT-BOOK OF ORGANIC CHEMISTRY. By DR. JOHANNES WISLICENUS. Translated and edited, with extensive additions, by W. H. HODGKINSON and A. J. GREENAWAY. New York: D. Appleton & Co. $5.00.

In the original this book appeared as a new edition of Strecker's "Organic Chemistry." Professor Wislicenus is one of the active chemists of the present time, and has added materially to our knowledge of carbon compounds. He belongs to the advanced wing of German chemical science. He is so thoroughly imbued with the ideas of "bonds," "structure," "valency," and the other outgrowths of modern organic chemistry, that he does not sufficiently recognize the importance of explaining these ideas and showing on what foundation they rest. In his preface, to be sure, he appears cautious. Thus this passage will be found: "In the present state of our science we cannot neglect the frequent use of structural formulæ based on the valency of the chemical elements. Their partial uncertainty and in many points tangible shortcomings need not prevent their use to some extent in a text-book, although their use requires care." This is excellent; but the author's caution forsook him as soon as he began his work, and we find at the very beginning a large number of entirely unexplained structural formulas, the sudden appearance of which is well calculated to dishearten even a brave, earnest student, while the only effect they can have on ordinary minds is hopeless mystification. Let us not be misunderstood. We do not object to the formulas as such. They are in most cases excellent tentative expressions of facts. They do not imply atom-juggling, as some suppose. They are really of very great value; but they are too strong food for infant chemists. To digest them fully, one must have had a preliminary training; severe indigestion will certainly follow the attempt to swallow them whole without this training.

It is scarcely necessary to refer to special cases to prove the correctness of the assertion that the author of this book presents the formulas prematurely. The entire book furnishes the proof. Some glaring cases may be found on page 58, where formulas are given for many cyanogen derivatives in regard to which our knowledge is very limited; on page 62, where certain complex compounds of hydrocyanic acid with metallic chlorides are dissected in such a way as to suggest a mass of knowledge which we do not possess; on page 94, which presents formulas for compounds of urea and oxide of mercury, etc. If the author had intended simply to inform his readers in regard to the latest views actually held concerning the structure of organic compounds, without showing exactly what the formulas mean, his book would necessarily be regarded as a success, but this was not his intention. The work was written for beginners, and for them, we submit, it is not suited. On the other hand, it must be acknowledged that it contains a large mass of valuable information systematically arranged and accurately stated, and if used in connection with

other books, as for example with that of Roscoe and Schorlemmer, or in connection with a good course of lectures, it will serve a good purpose. The translation is fair, though the translators are constantly under the influence of the German idiom. Stilted sentences are met with throughout the book. This, however, is almost inevitable, and we are not disposed to find fault, for, though the language is clumsy, the meaning is not obscured to any great extent. I. R.

NOTES.

On a new Gas Regulator.

In the description of a new gas regulator by Mr. Wilson in Vol. 3, No. 5, of this Journal, I note in the form of the apparatus a considerable advantage over that with which I had been familiar. If we combine this with that of Mr. Kemp, described in the Handbook of Chemical Manipulations by G. Williams, page 49, we shall have the desired apparatus, further simplified, while retaining all of the advantages of each. Such an arrangement may be represented by Figure 1, if we conceive the arm ED to be shortened, so as to

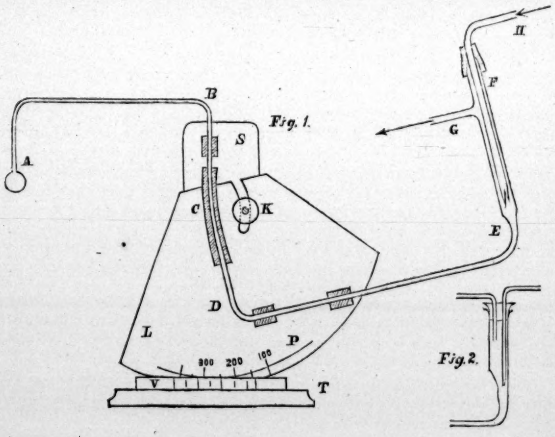


Fig. 1.

Fig. 2.

make CDEF form a simple U tube, and held rigid in a vertical position, and the tube H to slide up and down within the limb F, determining by its position the temperature to which the bulb A may be heated.

Having made an instrument of this kind, I found some difficulties in its working, which are avoided in the following simpler apparatus. This instrument, although rather bulky, may be quickly made, and not only enables one to keep an air, oil or water-bath at, approximately, a constant temperature, but also by a simple adjustment, to nearly eliminate variations due to the barometric pressure and the temperature of the laboratory, and to then adjust it for any desired temperature.

Its construction may be understood by reference to Figure 1, drawn about one-sixth of its size. A thermometer tube, bent at B, is supported by the stand ST. The thin board LK is fastened to the upright S by a screw at C, so that it may be revolved about C and be clamped in any desired position by the thumb-screw K.

The tube F, with inner diameter about 3 mm., is joined to a rather stout tube with small bore, and the latter is bent at E and D. The tube H is slid within the tube F, and is held firm by the rubber tube, which grasps them both and is tied. The tube ED is nearly filled with *clean* mercury, then joined to B by the heavy rubber tube C, about 70 mm. in length, leaving sufficient room between the tubes to allow of some motion, and then fastened to the board LK. A scale of equal subdivisions is attached to the strip of wood V, which is fastened to T. The lower end of H is made with a narrow slit in it, at least 5 mm. long, which is readily done by first piercing a hole and then drawing it out at that point.

The arm HE is brought to its lowest position, and by blowing into G, all excess of mercury is driven out through H. The arm is then raised until the lower end of the tube H just touches the surface of the mercury. A single mark made on the line P will be opposite to some division of the scale V, which latter will then serve as the index by which the several divisions of the scale P may be made by trials. If the barometric pressure decreases or the temperature of the atmosphere increases, this index point will be found further to the right, but may be employed with the scale previously made on P, with an error of less than 4 or 5 degrees. It will thus be seen that by raising the arm HE and fixing it in any position, gas can pass until the expansion of the air in the bulb A increases the pressure enough to force the mercury up into the tube F and diminish the passage of gas.

As the flame which is governed by this regulator may be extinguished, it is best to have a minute gas-jet constantly burning, and so placed that it will light the gas when it escapes again.

It is preferable to fuse the tube H to the top of F, and so avoid the rubber joint; on the other hand, the side joint G may be substituted by the arrangement indicated in Figure 2.

F. P. DUNNINGTON.

UNIVERSITY OF VA., *April*, 1882.

Artificial Quinine. (?)

"The discovery of H_2N has just furnished me with the means of realizing a synthesis desired by all chemists, and the object of a reward offered by the Society; this synthesis is that of quinine. I would at once communicate to the Academy the details of the very simple operation in which H_2N furnishes very pure sulphate of quinine, if it were not proper that I should first submit to medical proofs this sulphate, all the properties of which are identical with those of the sulphate prepared from quinquinia.

"The Academy, in accepting the deposit of the sealed packet accompanying this letter, will give me the opportunity to devote the necessary time to therapeutic studies. I will be grateful to them for it. E. J. MAUMENÉ."

The above note is taken literally from a recent number of the *Comptes rendus*. The remark "important if true" seems called for. Why, if this synthesis has actually been accomplished, the chemical world should be kept in suspense in regard to it, it is difficult to say. As we see it, there is something puerile about this mysterious sealed-packet method of announcing discoveries. If the depositor is not quite sure of his discovery, let him be silent: but if he is sure of it, in the name of all that is outspoken and truth loving, let him boldly proclaim it. The method seems specially adapted to the encouragement of abortions, which Heaven knows! are common enough without the necessity of being made respectable by a great Academy. I. R.

Processes for Direct Coppering of Castings of Iron and Steel.

F. WEIL gives an account of the processes devised by him for the direct coppering of castings of iron and steel without the use of any intermediate coating of plumbago or other material upon the surface of the casting.

The deposit of copper by this method is so homogeneous and so faithfully reproduces the most delicate details of ornamentation as to give to articles so coppered the artistic value of bronze, and at the same time is so firmly adherent that castings coppered by this process have remained exposed to the weather for ten years without requiring any retouching.

The alkaline organic baths used in the process present several advantages over the ordinary alkaline baths used in electroplating. The cyanides, which are both injurious to the health of the workmen and expensive, are replaced by organic acids or by glycerin, both of which are cheap and have the advantage of not being decomposed in the operation. Thus the baths require no renewal of organic material, and act continuously provided the necessary amount of oxide of copper is added from time to time. Finally, the well-known property of alkaline organic solutions of dissolving oxide of iron easily and rapidly without attacking the

metal itself, always renders the cleansing of the castings perfect, as the bath finishes the cleansing of articles before coppering them.

The process is carried on in three different ways according to local conditions and the different applications of the articles to be coppered.

The first method consists in plunging the articles in the bath in contact with strips of zinc. The coppering begins immediately, and, according to the alkalinity of the bath and the destination of the articles to be coppered, requires a variable time from a few minutes to several hours.

The second process, which has been employed with great success for coppering the street lamps of a large city, consists in placing in the vessel containing the bath and the objects to be plated porous jars filled with a strong solution of caustic soda, in which are placed plates of zinc connected with the articles in the bath by a coarse copper wire. The time required for depositing a moderately thick coating of copper, such as required by candelabra, etc., is very short.

The third process consists in the use of the same baths as in the first and second processes, in conjunction with a dynamo-electric machine.

The baths, as has been said, only require the addition of a certain amount of oxide of copper from time to time, and by a simple method of titration, also devised by M. Weil, the exact amount of copper oxide to be added can be readily and quickly determined.

These processes can also be applied to the deposition of all metals, such as nickel, cobalt, antimony, tin, etc., upon castings of iron and other metals.—(*Comptes rendus*, **93**, 1018.)

R. D. C.

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